COMPLEXES OF THE CUPROUS HALIDES
WITH DIALKYL ACETYLENES.

Thesis by
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In addition I wish to thank Professors E. R. Buchman and N. Davidson for their availability and for their interest and to acknowledge the heartening direction by Dr. E. W. Hughes in the structure problem.

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ABSTRACT

The complex formation of the disubstituted alkynes with cuprous halides has been investigated. No cuprous iodide-alkyne complexes have been observed. Many of the physical characteristics of the cuprous chloride-and cuprous bromide-alkyne crystalline complexes have been determined. These include the dissociation vapor pressures, the heats of dissociation, the compositions, their solubilities in excess ligand, and the densities and vapor pressures of their saturated solutions. In addition the vapor pressure lowering as a function of temperature for the saturated solution of the cuprous chloride 3-hexyne system has been investigated and compared with a theoretical model. A study of the vapor pressure lowering as a function of temperature for alkyne solutions of constant concentration for the cuprous chloride 2-butyne and cuprous chloride 2-pentyne systems suggests the presence of more than one complex species in solution.

A preliminary investigation of the absorption spectra indicates that the cuprous halide-alkyne complexes are strongly absorbent in the infrared and the ultraviolet.

The unit cell and space group of the cuprous chloride-2-butyne complex are given.

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PART I

COMPLEXES OF THE CUPROUS HALIDES WITH DIALKYL ACETYLENES.

A. INTRODUCTION.

The present work, which is primarily a study of the reactions of the cuprous halides with various alkynes in the aliphatic phase, is a natural extension of the studies initiated* by Winstein and Lucas (1) in 1938 on the addition complexes formed by olefins in aqueous silver nitrate solutions. The chemical nature of these addition complexes and their relationships to the reaction of olefins in the presence of certain metal salts have been long standing problems in chemistry and have in recent times received considerable attention. It is felt, however, that the subject has been adequately reviewed by Plesch (3) and Keller (4).

As in the case of the olefins, coordination of acetylene and its derivatives with cuprous and silver salts have been known for some time, however until recently little systematic work has been accomplished in this field. The production of colorless crystalline needles when acetylene is passed through an anhydrous alcohol-cuprous chloride mixture was first reported (5) by Hofmann and Kuspert in 1897. Their analysis indicated a composi-

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* In a prior paper by Eberz, Welge, Yost, and Lucas (2) the argentation constant of isobutylene was calculated but the study was mainly concerned with the hydration of isobutylene.

tion of $6CuCl \cdot C_2H_2$. Although very unstable the crystals were not explosive; however, in the presence of water or ammonia they decomposed readily to give an explosive red amorphous precipitate. A year later Chavastelon (6) described a colorless crystalline precipitate which was similar in most of its properties to that obtained by Hofmann and Kuspert. However, he prepared it at 10° by the solution of acetylene in dilute hydrochloric acid containing dissolved cuprous chloride. Chavastelon described these needles as prisms, 5-6 mm. long, belonging to the hexagonal or orthorhombic systems. Under very rigorous conditions he achieved their analysis and reported the composition of the complex as $2CuCl \cdot C_2H_2$. In this paper Chavastelon also reported the dissociation vapor pressure of the complex at several temperatures.

In two later papers, (7, 8) Chavastelon, following Berthelot (9), reported the existence of three different precipitates when acetylene was dissolved at different pressures in an aqueous solution of potassium chloride containing cuprous chloride. In addition to the two precipitates observed by Berthelot, viz., yellow crystalline needles and a purple amorphous material, he obtained colorless orthorhombic needles. Chavastelon expressed the results of his analysis in the following manner: $C_2H_2 \cdot (2CuCl \cdot KCl)_2$, yellow needles; $C_2H_2 \cdot 2CuCl \cdot CuO$, purple amorphous material; and $C_2H_2 \cdot 2CuCl \cdot KCl$, colorless crystals.

Manchot, Withers, and Oltrogge in 1912 suggested (10) the presence of a colorless 1-to-1 complex between acetylene and cuprous chloride in a hydrochloric acid solution containing only small amounts of cuprous chloride. Their suggestions were based on solubility measurements of acetylene as a function of the amount of cuprous chloride present. One might consider that this suggested complex parallels, but antedates, most of those studied by Keefer, Andrews, and Kepner (e.g. 11) in their work on the complex formation of olefins with cuprous and silver salts in aqueous solutions. Manchot and his coworkers found that at high cuprous chloride concentrations a colorless complex of the composition $2CuCl \cdot C_2H_2$ was precipitated and at low hydrochloric acid concentration a dark purple amorphous precipitate with the composition $Cu_2C_2 \cdot CuCl \cdot H_2O$ was formed.

Gilliland and his coworkers (12) determined the heat of dissociation, the dissociation vapor pressure, and the composition of the $2CuCl \cdot C_2H_2$ complex in equilibrium with solid cuprous chloride and gaseous acetylene. However, their molar ratio of acetylene to cuprous chloride in the complex varied from 0.462 to 0.535; furthermore, they reported the complex as having a purple color. Similar work was described in 1950 by Osterlof (13) who found three colorless addition complexes of acetylene with cuprous chloride in an alcoholic solution of hydrogen chloride. At -30° and 750 mm. pressure of acetylene, a

1-to-1 complex existed, and at 25° the 2-to-1 ($2CuCl \cdot C_2H_2$) and the 3-to-1 ($3CuCl \cdot C_2H_2$) complexes were present. For the latter two complexes he determined the dissociation vapor pressures at several temperatures.

Partial clarification of the reaction of cuprous chloride with acetylene under various conditions was given in four recent papers (14, 15, 16, and 17) by Vestin and his coworkers. The various compounds formed in the aqueous and solid phases in their studies have been included in Table 1 with the approximate conditions. Although many of their vapor pressure measurements were determined when the liquid phase was supersaturated with respect to one of the precipitates listed in Table 1, the measurements were reproducible. Furthermore the dissociation vapor pressure over the colorless addition complexes, $2CuCl \cdot C_2H_2$ and $3CuCl \cdot C_2H_2$, were approached from higher and lower pressures of acetylene. In previous investigations the approach was only from one direction (12, 13) or the method was undescribed (6). Vestin and his coworkers found that pure dry cuprous chloride did not react with anhydrous acetylene even when the partial pressure of acetylene was 10 atm.. The solubility of cuprous acetylide and silver acetylide in aqueous solutions containing dissolved cuprous chloride and silver nitrate respectively is probably due to the anion $Cu_2C_2 \cdot (CuCl)_6 \, Cl_2^{-2}$ (14) and cation $Ag_2C_2 \cdot Ag_6^{+6}$ (18). Definite evidence for less complex soluble addition compounds

Table 1.

Reaction of Cuprous Chloride with Acetylene at Room Temperature.[a]

Compound formed	Phase of compound	Color	Acidity	(CuCl)[b]	(Cl^-)[b]	P_A[c] atm.
$(H_2C{=}CH)C_2H$	gas		low	high	high	high
$(H_2C{=}CH)_2C_2$	gas		low	high	high	high
C_2Cu_2	solid, am.[d]	red	low	low	low	
$C_2Cu_2\cdot(CuCl)_n$	solid, am.[d]	violet	low	low	low	
$(CuCl)_6\cdot CuC_2\cdot(KCl)_2$	solid, cry.[e]	yellow	neutral	high	high	
$C_2H_2\cdot CuCl$	soln.	colorless	4M.[f]	medium		
$C_2H_2\cdot CuCl_2^-$	soln.	"	4M.[f]	medium	high	
$C_2H_2\cdot Cu$	soln.	"	4M.[f]	medium	low	
$C_2H_2\cdot 2CuCl$[g]	cry.[e]	"	high	high	high	0.57
$C_2H_2\cdot 3CuCl$[g]	cry.[e]	"	high	high	high	0.38

[a] Vestin and coworkers (14, 15, 16, and 17).

[b] Total concentration.

[c] Pressure of acetylene.

[d] am. means amorphous.

[e] cry. means crystalline.

[f] M. means molar.

[g] In equilibrium with solid CuCl.

involving the carbides such as $Ag_2C_2 \cdot Ag^+$ is not available even though solubility studies have been made (18, 19). Although the soluble cuprous acetylide complex has a very high molar extinction coefficient, concentrated silver perchlorate solutions of silver acetylide have a clear spectrum above 270 mμ. The crystal structures of the acetylide complex $Ag_2C_2 \cdot (AgNO_3)_6$, first prepared by Shaw (20), and of the acetylene addition complex $2CuCl \cdot C_2H_2$ have been described briefly by Osterlof (21). The complexes of silver acetylide with other silver salts have been reviewed by Vestin (18).

Prior to 1950 no quantitative work which is known to the author on the coordination of substituted acetylenes with cuprous or silver salts had been reported. Even the accounts of qualitative studies were very few in number. Yet aryl substituted acetylenes were known as early as 1912 to form colorless crystalline complexes with cuprous chloride simply upon mixing the reagents. This was the work of Withers and Oltrogge as described by Manchot (10). Table 2 lists the acetylene derivatives which reacted with cuprous chloride and their reported properties and Table 3 lists the related compounds for which no reaction was obtained. In these addition compounds, however, the nature of the binding of the triple bond to the cuprous chloride is obscured by the presence of other known electron donors.

Table 2

Acetylene Derivatives which React with Cuprous Chloride.[a]

Compound	Properties of complex formed.
$C_6H_5-C\equiv CH$	colorless crystalline needles, easily decomposed to starting reagents, reacts with water to form a colored salt
$CH_3-O-C_6H_4-C\equiv CH$	same as above
$(CH_2-O_2)=C_6H_3-C\equiv CH$	colorless crystalline needles
$C_6H_5-C\equiv C-I$	very narrow colorless needles
$C_6H_5-C\equiv C-Br$	large colorless tabular parallelepipeds, easily formed
$C_6H_5-C\equiv C-CO-NH_2$	fine colorless needles
$C_6H_5-C\equiv C-CN$	fine colorless needles
$HOOC-C\equiv C-H$	very small colorless needles
$C_2H_5OOC-C\equiv CH$	result unclear due to the formation of a brown precipitate

[a] Manchot, Withers, and Oltrogge (10).

Table 3

Acetylene Derivatives which did not React with Cuprous Chloride.[a]

$C_6H_5-C\equiv C-CH_3$

$C_6H_5-C\equiv C-C_6H_5$

$C_6H_5-C\equiv C-COOC_2H_5$

$CH_3O-C_6H_4-C\equiv C-CO-C_6H_5$

$CH_3O-C_6H_4-C\equiv C-C\equiv C-C_6H_4-OCH_3$

$(CH_2O_2)=C_6H_3-C\equiv C-C\equiv C-C_6H_3=(O_2CH_2)$

[a] Manchot, Withers and Oltrogge (10).

W.S. Dorsey, at this institution, gave an account (22) in 1950 of a 1-to-1 complex containing 3-hexyne and silver ion in the presence of aqueous silver nitrate using the distribution method (1, 2). His value for the association constant was confirmed by G. Helmkamp (23), who used a solubility technique and who extended the investigation to several other disubstituted alkynes some of which contain additional functional groups. Finally Comyns, also at this institution, isolated several crystalline complexes of disubstituted alkynes with silver nitrate and silver perchlorate from non-aqueous media (24).

B. APPARATUS.

Although much of the apparatus and techniques used in the present study are well known and practiced elsewhere, they are described here for the sake of completeness.

Constant Temperature Baths. Two constant temperature baths were used in the present study. Bath No. 1 was a "Sargent" water bath which consists of a pyrex jar 16 in. in diameter and 10 in. high equipped with cooling coils and with a pedestal containing heating and circulating units. Temperature sensitivity was obtained through the thermo-expansion of mercury in contact with a platinum electrode. The temperature was adjusted with the aid of a thumb screw attached to the electrode. The temperature could be maintained constant within ±0.02°. The bath level at high temperature was conveniently maintained with the aid of the 4-l. french separatory funnel having a large bore stopcock.

Bath No. 2 consisted of a jar 9 in. deep and 8½ in. in diameter equipped with a heating element, cooling coils, and a thermoregulator. This regulator depended upon the thermo-expansion of toluene. Electrical contact was achieved by the use of mercury. A coarse movement of a platinum electrode resulted in a very small temperature change (in the order of ± 0.01°). The precision obtained was somewhat greater than 0.01°. The bath was stirred with the aid of a propeller mounted on a "Cenco" motor.

A source of cooling water of inconstant temperature was supplied to the cooling coils of the baths from an "Aminco" refrigerated constant temperature bath.

Magnetic Stirrer. Magnetic stirring under water was conveniently obtained through the use of the apparatus depicted in Fig. 1. The rotating magnetic field was provided by a small "Norelco" horseshoe magnet mounted on the shaft of a 6-volt d.c. car-heater motor. The speed was adjusted with the aid of a rheostat. This stirrer was designed for use with the above mentioned constant temperature baths.

Shaker. A vibrating "Boerner" shaker* was used for the preparation of some complexes in ampoules and for the composition determination of certain complexes.

Cathetometer. The cathetometer used in all the measurements of pressure was made by the Fred C. Hensen Co.. It consisted of a counterbalanced traveling telescope mounted on a vertical heavy walled tube with a substantial three-legged base. Provisions were made for the leveling of the cathetometer. A 1-m. scale graduated in millimeters was attached to the vertical tube. In a private discussion, the manufacturer estimated the accuracy of the length of the scale and the position of the divisions to be within 0.1 mm. of their correct values. The fine adjustment was obtained with the use of a worm gear. Tenths of a millimeter were measured with a vernier scale.

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* Sold by Arthur H. Thomas Co., Phil., Pa..

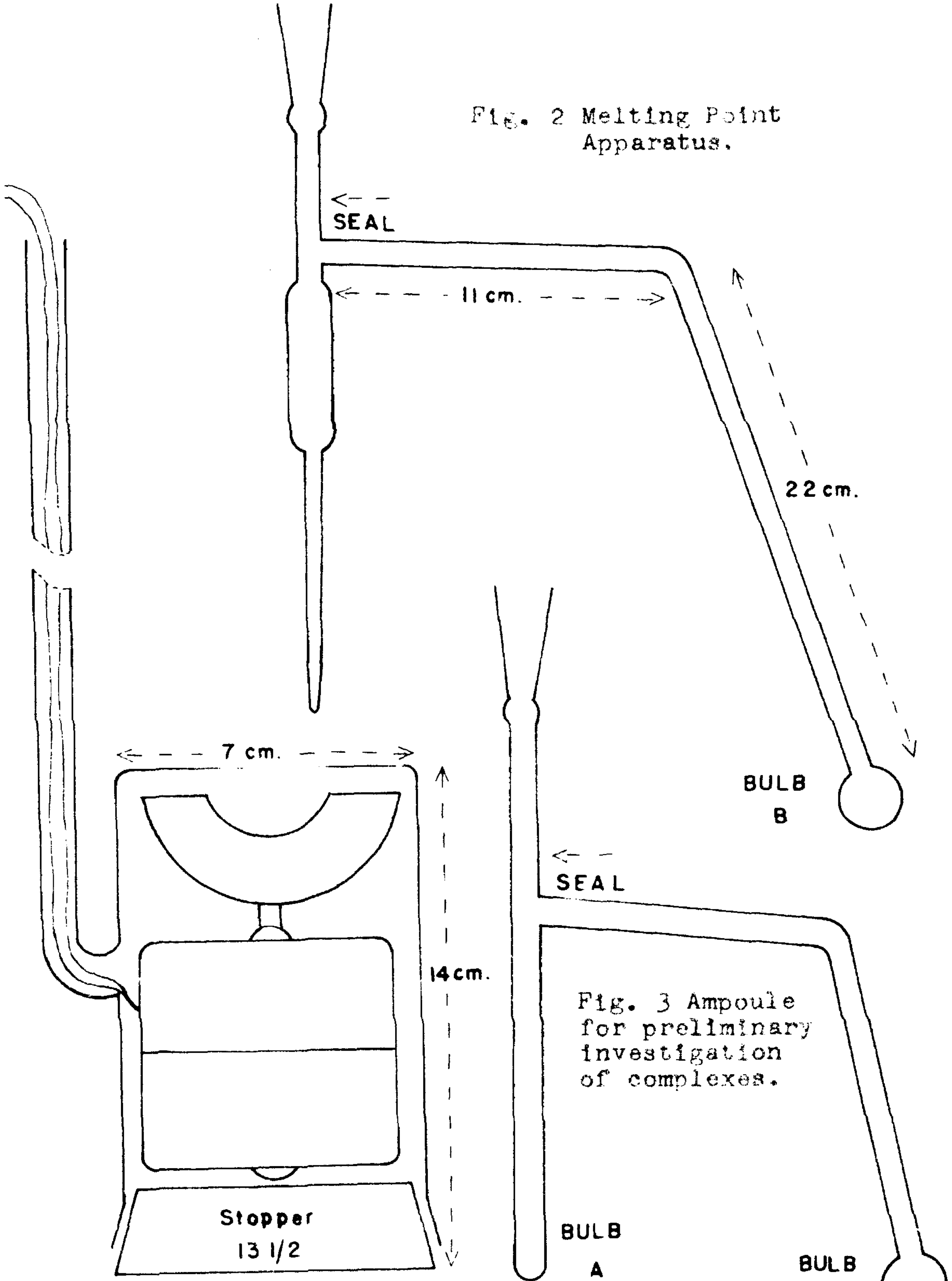

Fig. 2 Melting Point Apparatus.

Fig. 3 Ampoule for preliminary investigation of complexes.

Fig. 1 Underwater Magnetic Stirrer.

High Vacuum Apparatus: Introduction. A high vacuum apparatus is sometimes useful when it is found desirable to handle compounds that have appreciable vapor pressure (at least of the order of 1 mm. of mercury). The utility of the apparatus is particularly increased if it is necessary to exclude the atmosphere. The operations listed below are conveniently achieved on the high vacuum apparatus about to be described:

(i) quantitative transfer of a volatile compound between any two vessels in the system,

(ii) the determination of the molecular weight of a volatile compound by the measurement of a pressure and a volume,

(iii) purification by a volatile compound by fractionation and distillation,

(iv) determination of the vapor pressure of the volatile compound,

(v) interminable storage of a compound with the exclusion of all contaminants except mercury and glass.

It is appropriate to mention here that the apparatus was principally a chemical high-vacuum apparatus and that pressures of 10^{-3} mm. (ignoring mercury vapor pressure) are to be considered hard or high. The hardness of the vacuum was determined with the aid of a tesla coil. The author would also like to take this place to advise the reader that unless specifically stated otherwise 'distillation' should be interpreted as high vacuum distillation.

Some Details of Operation. A single stage mercury diffusion pump was used to produce the vacuum necessary; this was backed up by a Welch "Duo-seal" rotary pump. When nitrogen or air was being removed from the system, the mercury diffusion pump was bypassed to prevent the mercury vapor from being flushed into a trap or the pump. A rough vacuum "Cenco-hyvac" pump was used for the operation of the mercury reservoirs. To reduce the frequency of pumping a 5-1. flask was attached to the rough vacuum line as Fig. 4 shows. This usually made one evacuation a day sufficient. Nitrogen, advertised by the vendor* as 99.9 percent pure, was also used to operate the mercury reservoirs and to flush the high vacuum apparatus on certain occasions. The reader may correctly assume that all subsequent references to nitrogen gas refer to that variety mentioned above.

Some Details of Construction. The following details of construction are considered noteworthy since they have appreciably facilitated the fabrication and maintenance of the vacuum apparatus.

(i) Side arms were attached to the mainline prior to its permanent mounting on the bench. Additional side arms were added anticipating unknown future needs. Whenever possible the side arms entered the mainline from the top or the side, thus preventing free mercury from interfering

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* Linde Co..

VACUUM APPARATUS SCHEMATA

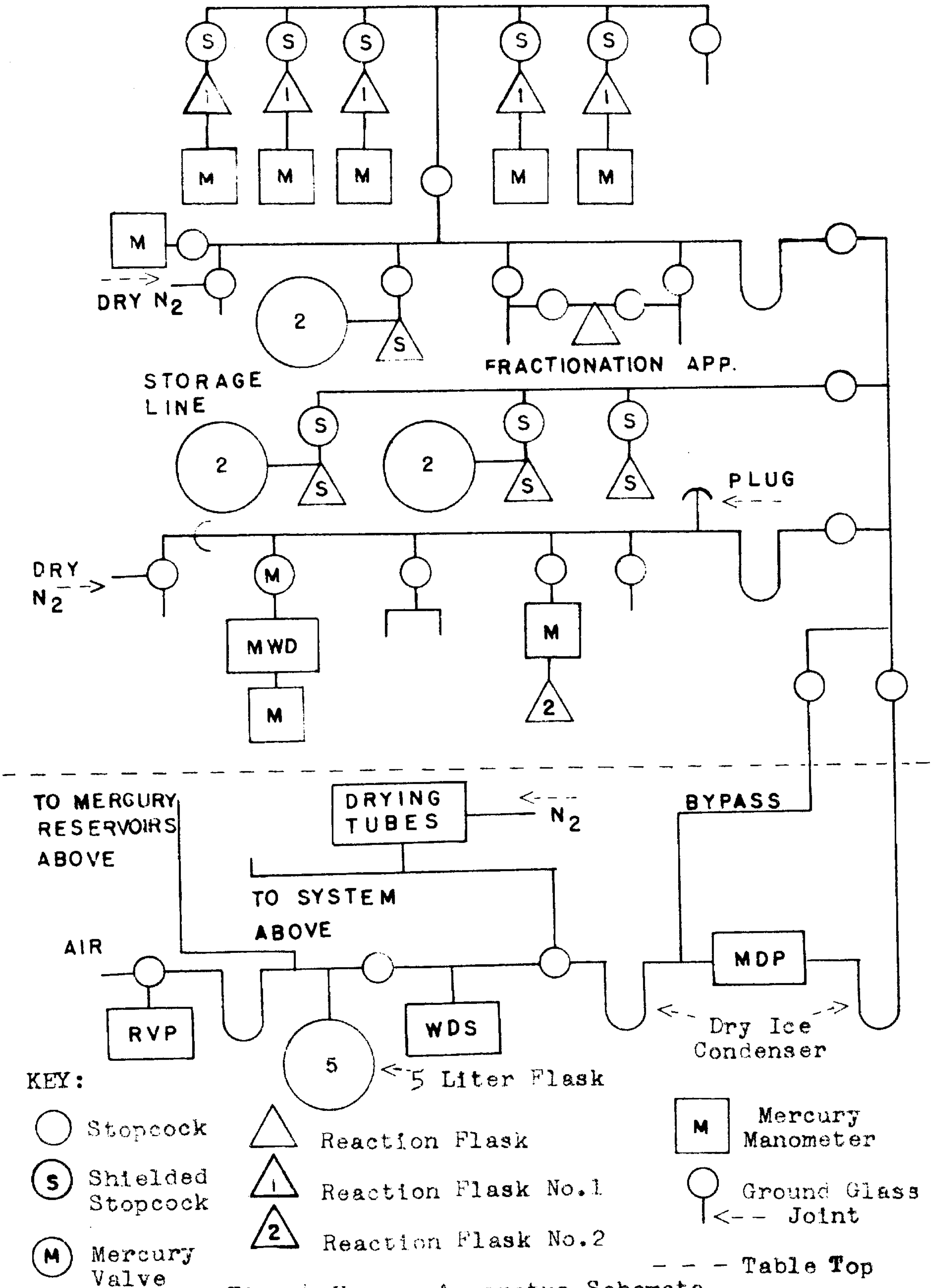

Fig. 4 Vacuum Apparatus Schemata.

with the operation of valves when the pressure differences were low.

(ii) Where possible the mainlines were mounted 30° from the horizontal. This prevented the formation of unwanted mercury pools. Provisions were made for the easy collection of the mercury.

(iii) The apparatus was constructed in such a way that unwanted material could be easily removed from all traps and all mainlines could be easily cleaned or washed out.

(iv) The leaching of grease from unshielded stopcocks by volatile solvents was noticeably reduced by having the approach to the stopcock from above.

Stopcock Grease. The greases found suitable for stopcocks were Apiezon "N" and "T". Apiezon "M" grease was found suitable for ground glass joints but not for stopcocks. "Celvacene" high vacuum, medium*, was satisfactory for neither stopcocks nor ground glass joints. The room temperature varied from 20° to 30°. The estimated average is 27°.

Valves. Vacuum stopcocks (using Apiezon "N" grease) in contact with the vapor of 2-butyne at room temperature for 24 hours developed leaks when cooled to -78°. The leaching powers of other alkynes reported in this study were similar. Hence, if the vacuum stopcocks are to be used under such conditions as above, then it is imperative that they be shielded from the vapor. Five different types

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* Consolidated Vacuum.

of valves have been constructed which are suitable for use in the presence of liquid solvents and their vapors.

Valve No. 1. Valve No. 1 is a valve described many times (25) and shown here primarily for comparison and completeness. It is the stopcock with the mercury cutoff in Fig. 9. The contact of the mercury with the grease is reduced by the use of the ground glass surface cutoff at the bottom of the mercury reservoir. The rod is normally forced down by extended rubber tubing. The tubing also serves the purpose of making the reservoir vacuum tight. When the rod is manually lifted the mercury level in the valve is raised or lowered according to the pressure in the reservoir. Rapid spoilage of the rubber tubing requires its frequent replacement; this is an awkward job when the reaction vessel cannot be disturbed.

Valve No. 2. Much like valve No. 1, this valve (Fig. 5) has a stopcock in place of the ground glass mercury cutoff. However, in the experience of the author, who greased the stopcocks of two such valves with Dow Corning high vacuum "Silicone" grease, proper degassing of the stopcock was not accomplished.

Valve No. 3. This valve, shown in Fig. 6, is easily constructed but requires considerable space. It was specially designed for slow removal of small amounts of gas from reaction flasks without fear of contamination of the system. This is achieved by lowering the mercury in the

SHIELDED VALVES

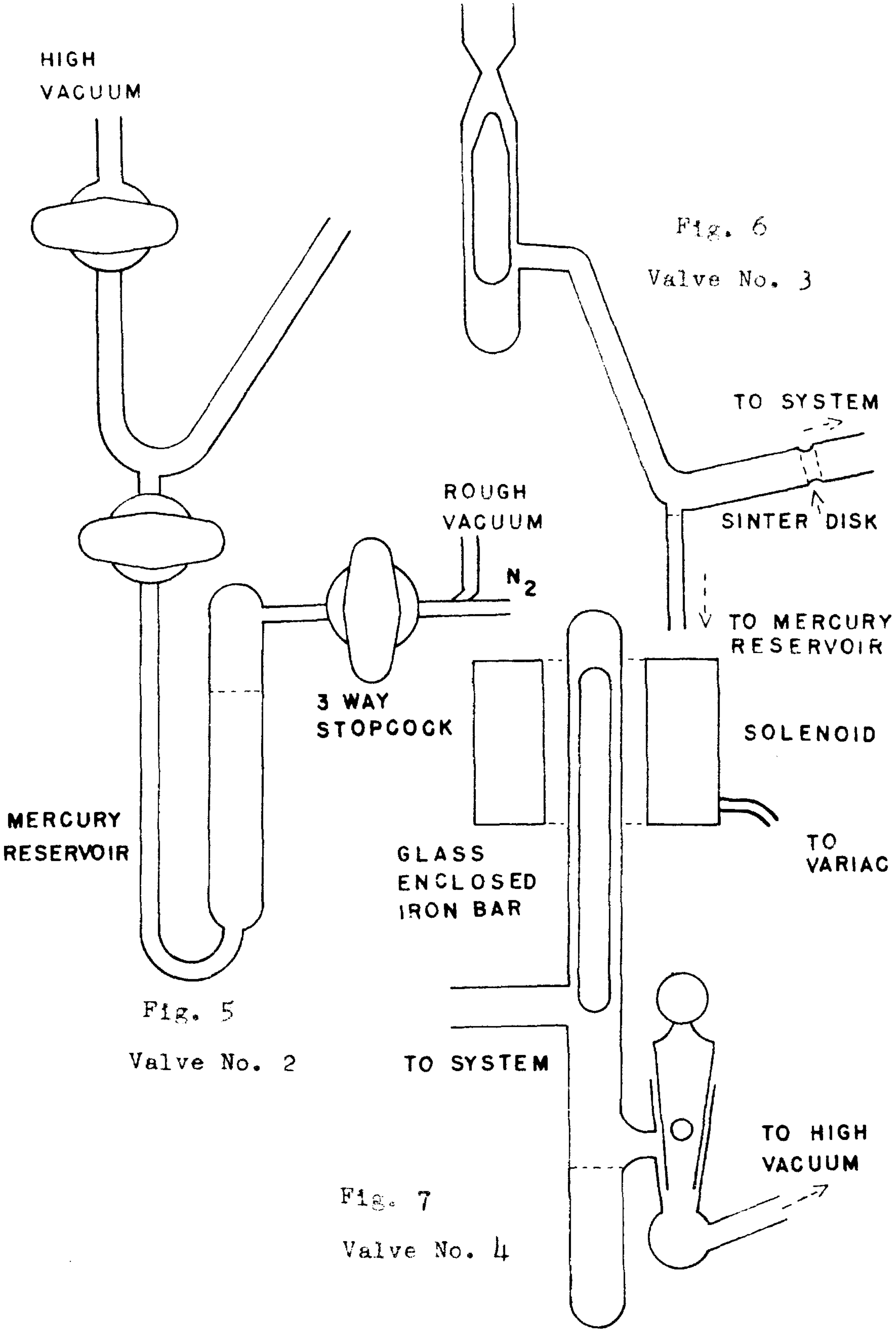

Fig. 5

Valve No. 2

Fig. 6

Valve No. 3

Fig. 7

Valve No. 4

valve to a position where a gas bubble appears and grows on the vacuum line side of the sintered disk. The pressure in the system should be at least 20 percent less than atmospheric if the valve is to be closed and not leak. The difficulty resides primarily in the fact that upon ambient temperature increases mercury expands and leaks into the reservoir, leaving insufficient mercury in the valve when the temperature subsequently decreases.

Caution should be exercised in the choice of sintered disks for this type of valve. The disk should not leak mercury under a pressure of 1.3 atmospheres or fracture or chip easily. In each No. 3 valve constructed, a 10-mm. diameter disk of medium porosity was used. The glass float was constructed of 8-mm. rod. The float is seated with gentle tapping.

Valve No. 4. For simplicity of construction and operation no previously described valve is comparable to valve No. 4 (Fig. 7). This valve requires no mercury reservoir for its cutoff properties. The mercury level is raised above the level of the grease in the stopcock simply by lowering a weight into a few cc. of mercury. The weight is an 11-cm. length of 1/4-in. "Swedish steel" enclosed with a few cc. of mercury in a section of 10-mm. pyrex tubing. Ample room was given for the expansion of the mercury enclosed with the iron rod. The weight is lifted by the gradually increasing magnetic field of a solenoid controlled with a variac. As the rod is lifted the mercury level in the 14-mm. cylinder is lowered and with tapping the stopcock is freed of mercury. The valve can be kept open indefinite lengths of time.

Mercury Float Valve. A mercury float valve has been constructed which opens readily with a pressure difference of one atmosphere across the seated floats. The use of sintered glass disks in the floats permits rapid equilibration of pressure across the valve when it is opened. Utilization of sintered disks for this purpose was first mentioned by A. Stock (27).

Construction. The valve is constructed of pyrex, and it is of sufficient simplicity that it may be completed by an amateur glass blower in a couple of hours (see Fig. 8). The ground glass seal is provided by the ground surfaces of a standard taper joint size 10/30. To construct the float the male part is joined to a sealing tube containing a medium 10 mm. diameter sintered glass disk. The other end of the sealing tube is pulled off and blown round so that the sealing tube terminates 24 mm. from the disk. Just below the disk a hole 7 mm. wide by 10 mm. long is blown in the side of the float. In order to facilitate the exit of the mercury from the interior of the float (hence away from the sintered disk) the lower edge of the hole is pressed inwards with a file, toward the axis of the cylinder. When this is not done only one side of the valve will open

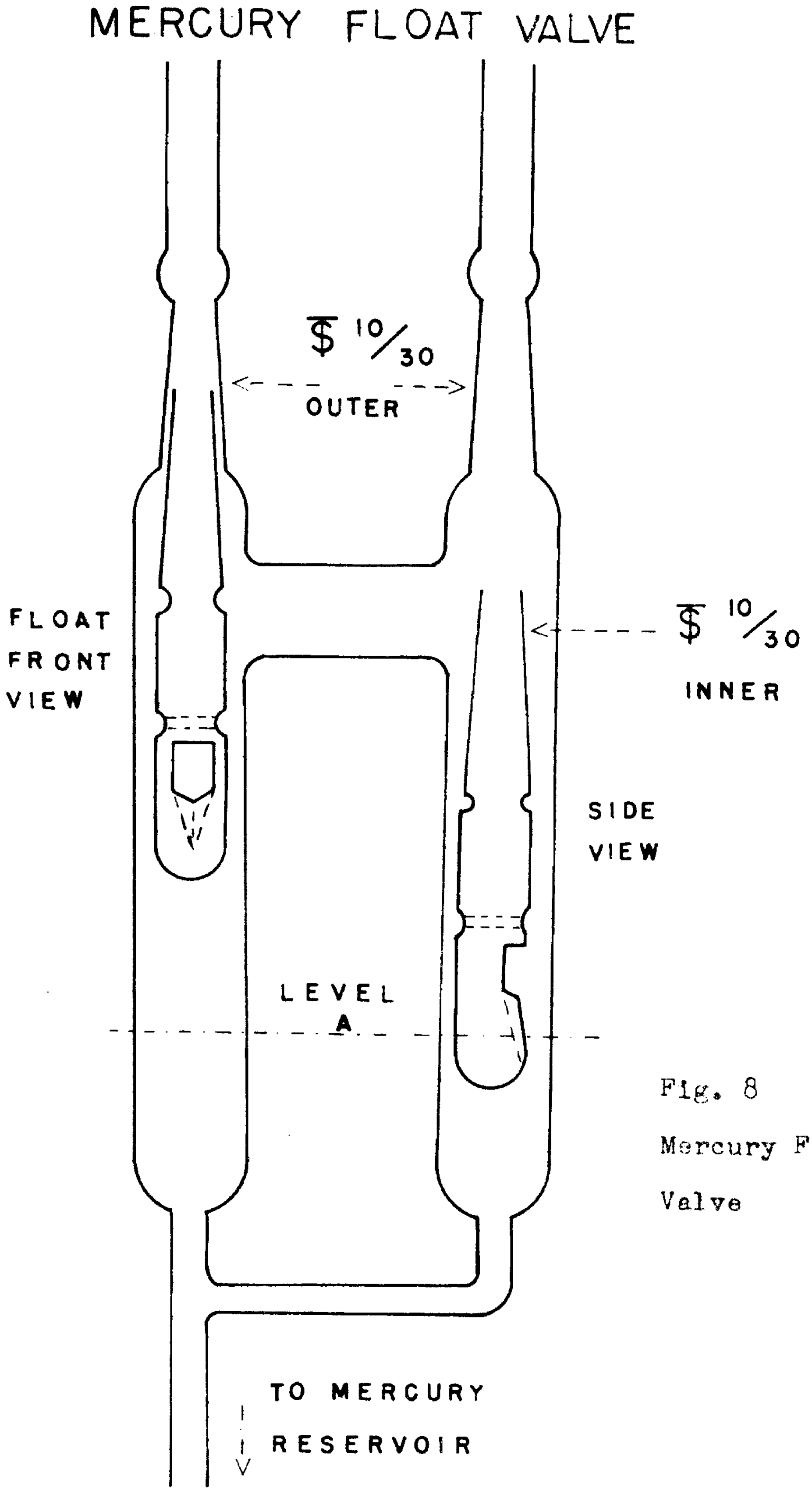

Fig. 8

Mercury Float

Valve

normally when the pressure difference is greater than about 6 cm. of mercury since surface tension effects do not permit the flow of mercury from the sintered disk on the low pressure side of the valve. The total length of the float is 75 mm..

The casing for the floats and the female part of the ground glass seal are constructed at the same time as the float. Two female members of the standard taper 10/30 joints are each carefully sealed at the beaded end of the ground glass surface to a length of 16 mm. tubing. To insure a ground glass seal and the concentricity of the parts a float (just after the sealing tube is joined to the male member of the ground glass joint) is lapped with a female member of the joint using a mixture of glycerol and 400-mesh carborundum as grinding compound. Once a satisfactory seal is obtained the members of the joints are no longer interchangeable. The rest of the construction is straightforward, as is indicated by Fig. 8. The valve then is carefully annealed.

Operation. The valve is opened by lowering the mercury to level "A". At this level the mercury protects the valve from injury by the falling float. The float on the high pressure side usually follows the mercury surface down. The pressure difference is equalized by diffusion of the gas through the sintered disk in the float on the low pressure side. When the pressure difference is approximately 2 cm. Hg the float on the low pressure side is freed by gentle taps on that side of the valve. The valve is closed by raising the mercury level and tapping gently as the floats seat.

The quantity of mercury used (*ca.* 33 ml.) could be considerably reduced by the use of a smaller sintered disk. Unfortunately they are not commercially available.

Storage Vessels. As indicated in Fig. 4 three storage vessels were constructed; two of them were provided with 2-l. flasks. Shielded valves of type No. 1 were employed. Hence it was possible to store for long periods of time the purified alkynes (3-hexyne, 2-pentyne, and 2-butyne) under oxygen-free conditions in a manner which was integral with the vacuum system and, hence, made them readily accessible.

Molecular Weight Determination Apparatus. Provisions have been made for the determination of the molecular weights of compounds volatile at room temperature (*i.e.* vapor pressure at least 10 mm.). The manometer was constructed of 14-mm. pyrex tubing. The valve used was the mercury float valve described above. The volume of the apparatus at zero pressure was 0.328 l. as determined with the aid of purified 2-butyne. If sufficient material was present rough measurements of vapor pressure could also be made.

Reaction Flasks. Reaction flasks, sometimes called equilibration flasks, were designed for vapor pressure

REACTION FLASKS

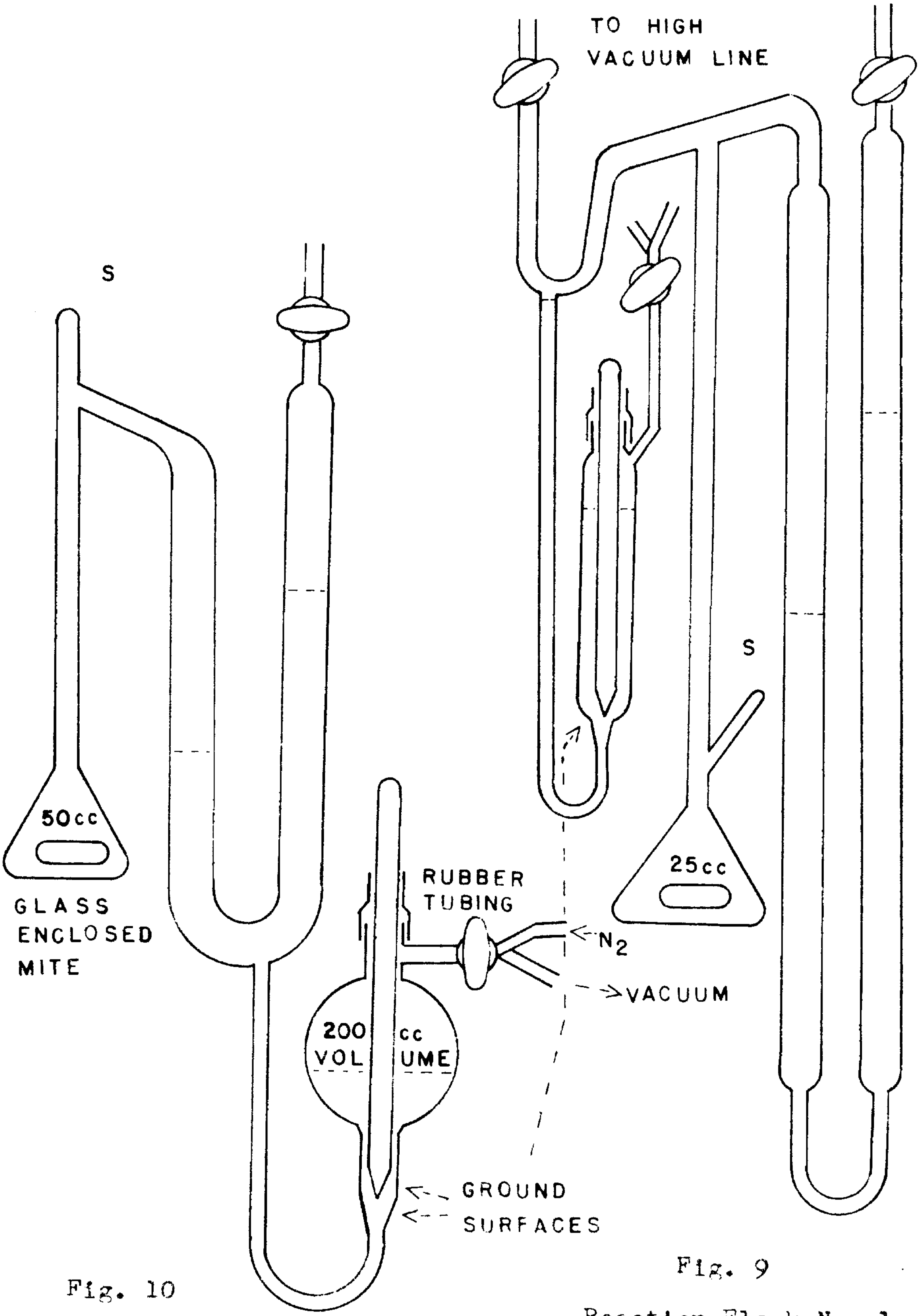

Fig. 10

Reaction Flask No. 2

Fig. 9

Reaction Flask No. 1

which protected the grease of the stopcock from the alkyne vapors.

This type was particularly convenient for use in systems where low pressures (ca. 100 mm. or less) were obtained. Samples of gas were removed without cooling the reaction flask itself by lowering the mercury in the manometer. With the aid of a reference point a system of constant volume could be obtained. The manometer was constructed of 20-mm. tubing.

Solids were introduced into both types of reaction flasks with a funnel through stem "S" indicated in Fig. 9 and 10. The maximum error of reading one column of mercury for both types of flasks was estimated at ±0.1 mm.. If this is combined with the maximum error estimated for the cathetometer then the total maximum error for a pressure determination is ±0.4 mm..

Sealing of Ampoules. Ampoules constructed from a clean section of 9-mm. pyrex tubing sealed to a standard taper 10/30 female joint, the inverted "U" type ampoule shown in Fig. 3, and the melting point apparatus Fig. 2 were always carefully sealed under high vacuum conditions, the joint removed and the seal annealed. This procedure was always unaccompanied by the charring of grease or organic compound or the destruction of any inorganic material unless specifically stated to the contrary.

Rough Vacuum System. A general purpose rough vacuum system was constructed and found to be of considerable use; however, the only feature of the system worthy of any note is the following pressure regulator.

Pressure Regulator. A new variation of the cartesian diver pressure regulator has been designed and constructed. The use of rubber stoppers and screw adjustments were avoided. Once initial adjustments of the mercury level (see Fig. 11) were made, no further adjustments were necessary. The cartesian diver was constructed of 20-mm. tubing and was removable. The inside diameter of the capillary measured about 0.7 mm.. The pressure in the reservoir (volume=50 cc.) controlled the movement of the float. This pressure was regulated by the stopcock to the system line and the stopcock to the atmosphere via a capillary. Failure to open the stopcock to the system and at the bypass at the end of distillation is not accompanied by the entering of mercury into inaccessible places. A paper giving the theoretical treatment of cartesian diver pressure regulators is that of Gilmont (28).

PRESSURE REGULATOR

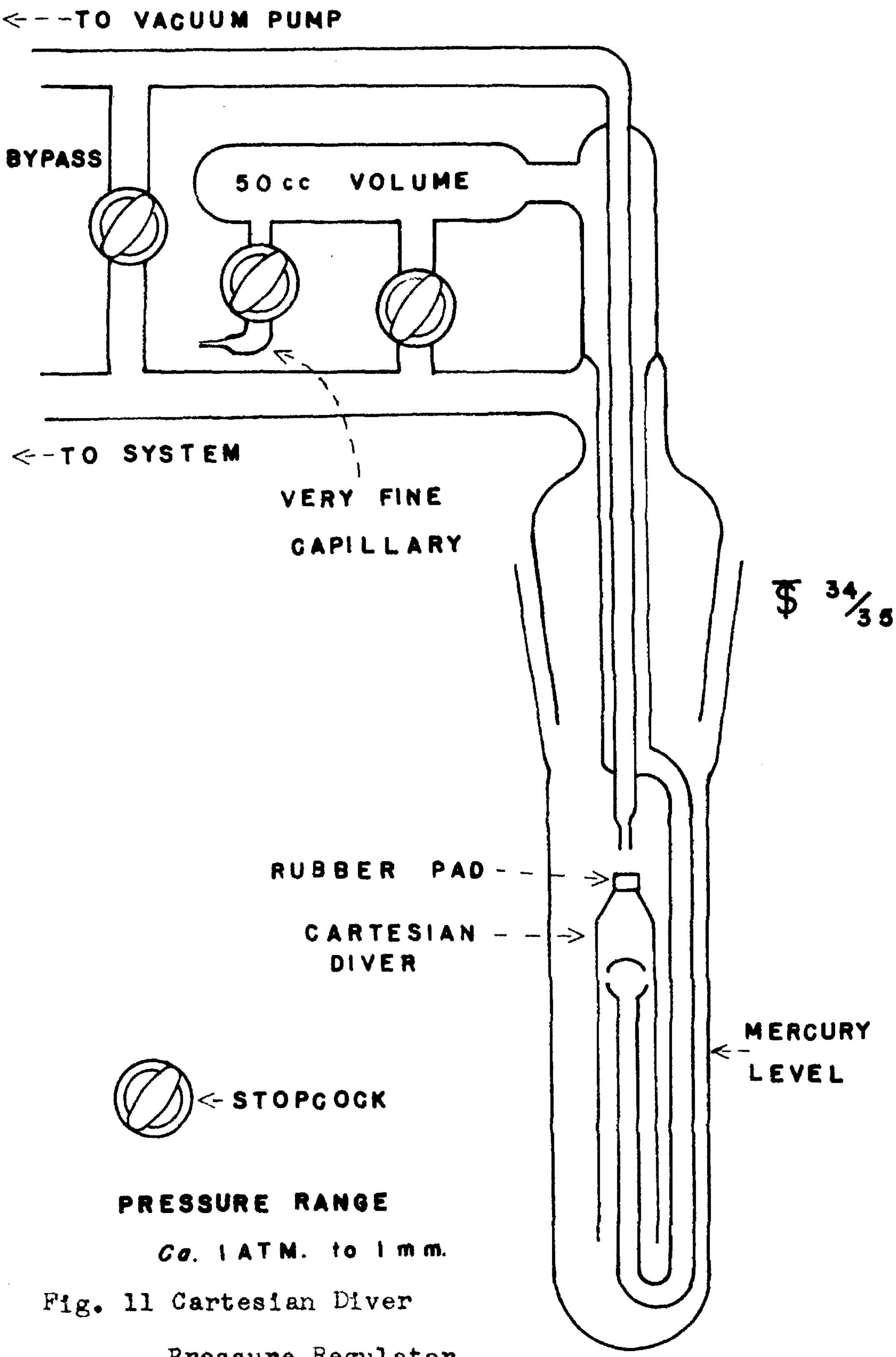

Fig. 11 Cartesian Diver
Pressure Regulator

C. REAGENT PREPARATION.

2-Butyne. This was obtained from Farchan Research Laboratories. The ampoule of alkyne as received from Farchan was cooled in an ice-water bath, opened, and transferred under nitrogen to a vessel containing freshly cut metallic sodium. This vessel was then attached to a high vacuum system, chilled in liquid nitrogen, and the alkyne degassed. The alkyne* was then allowed to warm to 0° with the metallic sodium in order to destroy any peroxides, water, or 1-butyne present. Since all of these processes involve the evolution of hydrogen, it was desirable to keep the hydrogen pressure as low as practical. This was achieved by cooling the vessel with liquid nitrogen and evacuating the gases formed every five minutes or so in order that the hydrogen pressure when the vessel was at liquid nitrogen temperature was of the order of 1 mm.. When the alkyne no longer reacted with sodium at 0° it was distilled to a clean flask and transferred under nitrogen to a 40-cm. helix packed column which had been flushed with nitrogen for at least one-half hour. The constant boiling (b.p. 26.9° at 747 mm; $n^{25}D$ 1.3890) second fraction was collected in an ice-hydrochloric acid bath at -17°. The condenser and the cold finger were cooled with a rapid stream of water at 3°. The column vent was protected by

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* Impure alkyne reacts with pure cuprous chloride to give a brown flocculent precipitate which obscures complex formation.

a glass "tee" through which nitrogen was flowing. The nitrogen flow rate was adjusted until bubbles formed at a slow rate from a piece of tubing immersed a centimeter into a container of water. The second fraction was transferred under nitrogen to the high vacuum apparatus and again treated with sodium. Little or no reaction was observed. The sodium treatment was used for each of the alkynes prepared both before and after distillation under nitrogen. The purified 2-butyne was then stored.

2-Pentyne. Although most of the 2-pentyne used was from Farchan an appreciable fraction was from some 2-pentyne which Comyns had recovered from solubility experiments. Generally the purification* of the 2-pentyne was similar to that described for 2-butyne except that two distillations under nitrogen were made instead of one; in the first, fractionation was accomplished with a 35-cm. Vigreux column and in the second, with a 40-cm. helix packed column. In each case the second fraction was collected. The physical properties were b.p. 55.3-55.4° and b.p. 55.4°(743 mm.), $n^{25}D$ 1.4005. It was not necessary to use 3° water for cooling. However, the distilled alkyne was collected at 0°.

3-Hexyne. The source and purification of 3-hexyne was essentially the same as for 2-pentyne above. The physical

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* The residue from the sodium treatment would in some cases, usually after treatment of impure 2-pentyne, ignite spontaneously in air after a short induction period.

properties were b.p. 80.3-80.7°(750 mm.), $n^{25}D$ 1.4090 (second fraction 35-cm. Vigreux column) and b.p. 80.6° (749 mm.), $n^{25}D$ 1.4090 (second fraction 40-cm. helix packed column).

Unless noted otherwise the alkynes used in the following experiments were purified as above and stored in the special vessels described on page 22.

Cuprous Chloride. Pure white cuprous chloride was prepared in a manner similar to the following example. Reagent grade cuprous chloride (green, 28.6 g.) was dissolved in approximately 50 ml. of reagent grade concentrated hydrochloric acid. The dark brown opaque solution formed was filtered through a medium sintered disk Buchner funnel. The filtrate was then added to 4.1 of distilled water through which nitrogen had been bubbled for one-half hour. White cuprous chloride was precipitated and the supernatant liquid had a light blue color. When the precipitate had settled the aqueous phase was removed by decantation and the precipitate was collected in a 50-ml. centrifuge tube. After centrifugation, the remaining solution was removed by decantation and the precipitate washed once with nitrogen-bubbled water and again collected by centrifugation and decantation. When the precipitate was redissolved in concentrated hydrochloric acid a yellow solution was formed which gradually became brown as more cuprous chloride dissolved. The brown solution, after filtration, was diluted and again gave a very pale blue solution and a white precipitate. The procedure was repeated for the third time and the collected precipitate washed twice. Immediately after the final decantation the centrifuge tube with the cuprous chloride was introduced into one side of an inverted "U" system of glassware connected to the high vacuum apparatus. The inverted "U" was detachable from the apparatus and was comparable in appearance to that in Fig. 29. After the system had been evacuated for about 7 minutes the stopcock of the inverted "U" was closed and the system removed from the vacuum line. The other side of the "U" was a long section of 25-mm. tubing. This side of the inverted "U" was immediately cooled and maintained at liquid nitrogen temperature. After 22 hours of drying, 4.1 g. of pure white cuprous chloride was obtained. Once established as a practical procedure the above method was followed except as indicated in the additional notes and comments below:

(i) This method of purification insures the absence of all contaminants except in trace quantities. Any hydrochloric acid present with the final cuprous chloride sample was removed with the water;

(ii) The hydrochloric acid present in the precipitate delays air oxidation of the cuprous chloride (29). In neutral and basic solutions in the presence of air, the cuprous chloride precipitate immediately turns yellow.

For this reason the precipitate was washed only twice. For the same reason the precipitate was collected as soon as possible after decantation. A 4-l. beaker rather than a large Erlenmeyer flask was used to contain the nitrogen-bubbled distilled water, as immediate collection of the sample was easier from the beaker.

(iii) Prior to the final filtration the Buchner funnel and the filter flask were rinsed with concentrated hydrochloric acid. The final concentrated hydrochloric acid solution was clear light yellow. However, at the air-liquid interface brown discoloration was always present. The discoloration increased with time and stirring. Because of its presence, purification beyond three precipitations availed only the loss of the cuprous chloride.

(iv) Upon drying with liquid nitrogen for approximately 22 hours the surface of the precipitate was discolored with green to brown markings. However, in the presence of air this discoloration disappeared in about 2 minutes leaving a pure white surface and, upon evacuation, would not reappear. In collecting the sample the surface was scraped off the hard mass of cuprous chloride in order to remove the discolorations. Before use the precipitate was powdered with a mortar and pestle. The yield of a purified material depended upon the condition of the starting material. The yields were usually low (14 percent) because of the practices mentioned above. When white cuprous chloride was available from previous purifications only two precipitations were made when the discoloration of the initial hydrochloric acid solution was slight.

(v) The method of drying the collected precipitate with ordinary anhydrous ethanol and ethyl ether followed by evacuation (13, 30) gave unreliable results possibly because the solvents were not anhydrous. This method of drying usually produced a blue sample. The same result was obtained when the sample was dried in the high vacuum system without the liquid air condenser.

Cuprous Bromide. The purification of cuprous bromide was very similar to that of cuprous chloride. Reagent grade cuprous bromide (blue-white) was dissolved in reagent grade 48 percent hydrobromic acid. The solutions formed varied in color from a dark opaque purple to a clear purple as the sample increased in purity after the precipitations. The samples collected by decantation and centrifugation were pure white. The final precipitation and drying of the collected sample was achieved in darkness as this method seemed to give rise to the whitest cuprous bromide. The discoloration of the surface of the dried material was similar in its color and behavior to that of the cuprous chloride. The final yields of the cuprous bromide were also low. However, more often than not, the dried cuprous bromide was not pure white but was tinted a very light blue. Moreover upon introduction of a powdered sample of cuprous bromide into a high vacuum system the blue color was replaced by a very light yellow one in one-half hour. This effect was not noticed for the cuprous chloride samples.

A sealed ampoule containing a purple solution of cuprous bromide in hydrobromic acid and reagent grade copper pellets became colorless in three days.

Cuprous Iodide. The preparation of cuprous iodide followed essentially that given by Hammock and Swift (31). The color of the final product was buff. Attempts to prepare white cuprous iodide with hydriodic acid as above were unsuccessful. The cuprous iodide was stored in an evacuated desiccator and removed as needed.

Stability of the Cuprous Chloride and Cuprous Bromide. Only pure, freshly prepared, cuprous chloride and cuprous bromide give clear solutions when dissolved in excess pure alkyne. These cuprous halides, when they had been exposed to the atmosphere after purification as much as four hours dissolve in pure alkyne in the absence of air to produce filmy white precipitates in small quantities, which in about a week's time were transformed to denser green precipitates. Pure cuprous chloride and cuprous bromide which had been stored in an evacuated system immediately after exposure to air gave similar cloudy solutions in some cases.

Although the contamination would not be serious for the purposes of many of the experiments to be described it was considered that the uncertain nature of the contaminant rendered it undesirable. For this reason, unless stated to the contrary, it is to be assumed that all cuprous chloride and cuprous bromide used was freshly prepared as described above and removed from the presence of air within an hour's time.

For purposes of manipulation it was necessary in some cases to grind the dried cuprous halide. Powdered samples of pure material gave clear solutions when dissolved in the pure alkynes immediately after grinding. Ground samples, however, are less stable in air than the unground cuprous halides.

Table 4 lists the increase in weight and the change of color of two ground cuprous chloride samples in the presence of air as a function of time. The samples were stored in weighing bottles beneath inverted beakers and were exposed to indirect lighting. As might be expected the change in weight was not a sensitive test for the presence of small amounts of contaminants due to the oxidation of the samples. Although only a white sample of cuprous chloride was considered pure, the color alone was evidently not a sensitive criterion of purity.

Table 4

Increase in Weight of Ground Dry Cuprous Chloride Samples in Air as a Function of Time.

Sample Weight = 1.4507 g.
Drying Time = 48 hours

Time of exposure. days	Weight Increase. mg.	Color
0.0	0.0	white
0.2	0.1	
1	0.9	
2	1.4	
3	1.3	
4	1.4	
5	2.2	
6	2.1	
7	2.9	
8	2.8	
12	3.7	very light green
13	4.1	
14	4.1	
16	4.2	
18	4.9	
38	6.1	light green

Sample Weight = 1.8586 g.
Drying Time = 15 hours

Time of exposure. days.	Weight Increase. mg.	Color
0.0	0.0	white
0.17	0.1	
1	0.6	
2	0.7	
3	1.3	
6	2.2	
7	2.5	
8	2.4	
10	2.7	
12	3.5	
32	5.3	very light green

D. GENERAL PROPERTIES OF THE CUPROUS HALIDE-ALKYNE COMPLEXES.

Preparation. Cuprous chloride and cuprous bromide readily dissolve in excess liquid alkynes (2-butyne, 2-pentyne, and 3-hexyne) exothermically to form clear colorless solutions. If sufficient cuprous halide is present clear colorless crystals appear upon warming the solutions to about 35° and allowing to stand at 0° for an hour. The 2-pentyne complexes are occasionally somewhat more difficult to crystallize. The solubility of the crystalline complexes in the liquid alkyne increases with the temperature in the range 0° to 30°. Addition complexes containing cuprous iodide and an alkyne have not been observed. The solubility of cuprous iodide in the alkynes studied appears to be very slight.

Experimental. Under airfree conditions nine ampoules were sealed at low temperatures; each contained a different combination of 1-2 ml. of alkyne (2-butyne, 2-pentyne, or 3-hexyne) and sufficient cuprous halide (cuprous chloride, white; cuprous bromide, white; or cuprous iodide, buff) to form crystalline complexes at room temperature. In each case the liquid was clear and colorless. Cuprous chloride and cuprous bromide formed clear colorless crystals with each alkyne. However, no crystals were observed in any ampoule containing cuprous iodide, even though the ampoule was shaken at 0° for two days and allowed to stand at -78° for five days (2-butyne freezes at -32°). Nevertheless the cuprous iodide in the ampoule containing 2-pentyne underwent at ambient temperatures a gradual lightening of color during the passage of a year to a much lighter buff.

Stability of the Crystalline Complexes. Like a crystalline hydrate loosing its water of crystallization at constant temperature these molecular complex crystals effloresce when the pressure of the alkyne falls below a certain value. In the absence of air the alkyne can be recovered quantitatively from both the crystalline complex and the solution leaving behind the pure cuprous halide. The dissociation of the solid complexes into their molecular components occurs with such extreme ease in the cases most intensively studied that normal methods of manipulation are precluded. The study of the complexes is further complicated in the presence of air, since the finely divided cuprous halide is easily oxidized and the liquid alkyne is converted after a period of time into peroxide. Attempts to isolate the solid complexes in the presence of air results in a dull white, or yellow, opaque mass quite different in appearance from the clear, colorless, crystalline complex.

In the attempted storage of the dry cuprous bromide-3-hexyne complex in a stoppered test tube, a different type of decomposition occurred. Within 36 hours three brown spots containing some liquid had developed, apparently nucleated at the storage vessel wall. Transference of some uncontaminated complex to another clean storage vessel was accompanied in a similar period of time with the appearance of other nuclei of decomposition at the wall of the new vessel. Hence, it was apparent early in the study that high vacuum techniques of manipulation of materials would be advantageous.

Stability of the Complexes in various Solvents. The crystalline complexes may be dissolved in and recrystallized from mixtures of pure alkyne with carbon tetrachloride, heptane, or ether. However, the pure solvents (unmixed with alkyne) readily destroy the complexes leaving most of the cuprous halide undissolved. If cuprous chloride or cuprous bromide is shaken with one of the mixtures mentioned above in sufficient quantities, the complex is precipitated or can be crystallized from the solution at lower temperatures. Similarly the complex can be formed in the presence of water. However, the slow oxidation of the cuprous halide in the aqueous phase brings about the ultimate destruction of the complex when air is not excluded from the system.

Stability of the Complexes at High Temperatures. When a sealed ampoule containing the crystalline complex in the presence of sufficient alkyne saturated with a complex is warmed above room temperature the crystalline complex dissolves to form a clear solution. However, at a higher temperature a white* precipitate which appears clear under magnification (x10) is formed. The temperatures at which this occurs depend upon the system. For the cuprous chloride 3-hexyne system this precipitate is present at about 44° and is present in all six systems mentioned above at 100°. In the cuprous chloride 2-butyne and the cuprous chloride 2-pentyne systems the amount of precipitate present at 100° gradually increases during the first one-half hour. When these precipitates are isolated they are found to be masses of clear crystals with poorly developed faces stable at high temperatures (320°) and low pressures. Since these precipitates redissolve at room temperature to give molecular addition complexes the precipitates are considered to be the original cuprous halides. Qualitative experiments lead the author to believe that even at 100° cuprous chloride and cuprous bromide are soluble to an appreciable extent in the three alkynes.

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* In certain cases (2 ampoules containing cuprous chloride and 2-butyne and 2 ampoules containing cuprous chloride and 2-pentyne) the precipitate at 100° was not a white solid but a clear orange-to-red solid. These colored crystals were in all other aspects similar to the white solid. Their occurrence was rather striking since the solutions were colorless before and after their formation. When the ampoules were cooled, the red crystalline precipitates dissolved to give colorless solutions. Except in one case (an ampoule containing cuprous chloride and 2-pentyne) the solutions were clear and free of foreign matter. In the excepted case a filmy green precipitate, indicative of cupric compounds, was present in very small quantities.

Reaction of Dissolved Complexes with Metallic Zinc. Nine ampoules were prepared as above and sealed at low temperatures. In addition to the normal content, however, each contained a bright 1-in. strip of reagent grade metallic zinc. When allowed to warm to room temperature the solutions of cuprous chloride and cuprous bromide, saturated and unsaturated with respect to the crystalline complex, immediately plated strips of metallic zinc with heavy coats of copper. Mixtures of cuprous iodide with the alkynes were much less active in the substitution reaction. The distinction between cuprous iodide and cuprous chloride and cuprous bromide is brought out in Table 5 where the appearance of the zinc strip is indicated as a function of time. The reactions for the changes of color of the cuprous iodide are not understood in terms of the simple structural picture for the different alkynes. All solutions and crystalline complexes remained colorless in the presence of the zinc strips.

Conductivity of Concentrated Solutions. Concentrated solutions of cuprous chloride and cuprous bromide in the various systems studied are assumed to be non-conducting at room temperature; however, attempts to measure the conductivity were made for only one system, cuprous chloride dissolved in 3-hexyne. That other solutions are non-conducting is surmised from their similarities to the cuprous chloride 3-hexyne solution. It was considered

Table 5

Plating of Zinc Strip under Oxygen free Conditions.

	1/2 hr.	1 day	4 days	1 year
Cuprous Chloride				
2-Butyne	I[a]	H	H	H
2-Pentyne	I[b]	M		M
3-Hexyne	I[b]	H		H
Cuprous Bromide				
2-Butyne	I, V H	V H		V H
2-Pentyne	I	H		H
3-Hexyne	L	H		V H
Cuprous Iodide				
2-Butyne	I, V L	L		L[c]
2-Pentyne	none	S		H[d]
3-Hexyne	none	none		none

I, immediate plating; V H, very heavily plated; H, heavily plated; M, medium plating; L, lightly plated; S, slightly plated, edges only; [a] zinc strip plated before all alkyne had melted; [b] chips of copper plate are present in solution; [c] cuprous iodide is a light buff color; [d] cuprous iodide is white.

desirable to measure the conductivity of these solutions in view of the ease with which zinc replaces copper in solution.

Experimental Details. 3-Hexyne (7.28 g.) freshly treated with sodium, was distilled into an ampoule containing 2.13 g. of cuprous chloride. The ampoule was sealed and the cuprous chloride dissolved to form a 26 mole percent solution* of cuprous chloride. The conductivity cell, cleaned and dried, was filled with alkyne solution and placed in a constant temperature bath at 25.0°. The bright platinum electrodes were approximately 1 cm. square and were placed 1 cm. apart. A student setup equipped with high frequency alternating current and ear phones was used.** The resistance of the solution in the cell was beyond the range of the apparatus: it was also beyond

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* The solution, while clear, was tinted a light pink. This color was often observed in solutions at the beginning of the investigation and is believed to be due to the presence of an impurity in the cuprous halides. After the methods of cuprous halide purification had been established the appearances of the pink solutions were of rare occurrence. It is interesting to note that when these colored solutions are cooled below 0° the color disappears and reappears upon warming to room temperature. Apparently this phenomenon is reversible as it may be repeated as often as desired. The color is not removed by filtration or by centrifugation with a clinical centrifuge. It has been observed under a variety of conditions, usually in the presence of oxygen.

** This experiment was performed with the aid and friendly interest of Professor Badger.

the range of a "Simpson" test meter. The connections of the cell were intact since a 0.1 molar potassium chloride solution was found to be conducting before and after the experiment.

<u>Notes on the Individual System</u>. Detailed information about the addition complexes will be listed by the system after experimental details have been mentioned.

<u>Experimental Details</u>. Photomicrographs of the crystalline complexes mentioned above had been taken. The lateral magnification of the photomicrographs given here is 100. Some of the crystals were photographed in ampoules. Others were photographed in the presence of their mother liquor contained in a deep cylindrical well of a 1/4-in. thick microscope slide. Loss of alkyne by evaporation was minimized by a glass cover over the well.

The photomicrographs were taken with a Zeiss "Ikon" camera (Nr. 16765). The film used was Kodak "Portrait Panchromatic", 9 x 12 cm.. The exposure time was approximately 1.5 sec..

The ordinary method of determining the melting or decomposition point of crystalline materials are inapplicable. Reproducible melting and decomposition points can be made with the apparatus shown in Fig. 2. These melting point tubes were constructed from 9-mm. tubing and a 15-ml. pyrex test tube drawn out to form a thin walled capillary 1 mm. in diameter.

The crystals were prepared in the capillary as follows:

about 0.3 g. of inorganic constituent was placed in the test tube section by means of a long stem funnel. The apparatus was then attached to the vacuum system and the alkyne (0.5-1.0 ml.) distilled into bulb "B". After the melting point apparatus had been sealed and the joint removed the alkyne was allowed to react with the metal salt in the test tube section of the apparatus. The excess pure alkyne was then distilled into "B" while the temperature difference between the capillary and "B" was carefully controlled so that dry but undecomposed crystals were in the capillary. The capillary was then introduced into a melting point bath and the bulb "B" placed in a constant temperature bath. The temperature of the melting point bath was increased at the rate of 0.3° per min. and the effects noted. The temperature of "B" was recorded.

System; Cuprous Chloride 2-Butyne. Clear flat plates of the cuprous chloride-2-butyne complex can be grown from solution by evaporation of the alkyne. Two crystalline forms have been observed, parallelograms and rectangular plates. The tabular nature of the observed crystals has probably been exaggerated by the presence of the surfaces of the mother liquor and the container. Both habit modifications extinguish between crossed Nicol prisms when the long edge of the crystalline plates is parallel to the electric vector.

Fig. 12 shows a photomicrograph of a crystal of the cuprous chloride-2-butyne complex in the presence of its mother liquor. Multiple growth layers of different thicknesses are evident (32). These layers are in the form of closed loops. The smallest step height visible would correspond to a dislocation (or dislocations) of multiple strength, since the largest unit cell dimension of this complex is 13.00 A (see page 186). The identity of the face parallel to the film is uncertain, but it is certainly of a form (hol) since the crystal is monoclinic. If the dislocation (or dislocations) was parallel to the n-glide and perpendicular to the crystal face then the latter would be identified as the (101) face. Growth layers were not observed for crystalline complexes of other compositions.

When the glass cover of the well was removed and the mother liquor allowed to evaporate the crystalline complex began to decompose. Fig. 13 shows the same crystal in Fig. 12 20 sec. after the well cover was removed. The dark areas are cuprous chloride from the decomposed complex. A needle like modification of the cuprous chloride-2-butyne complex has been observed in an apparatus like Fig. 2, in which some charring took place when it was sealed. An x-ray examination showed that they had the same cell size and space group as the tabular crystals.

The dry crystalline complex is stable until the temperature is 69.5^{0} when bulb "B" of the melting point apparatus is at 25.0^{o}. At 69.5^{o} the small poorly-formed crystals show evidence of decomposition. The well-formed crystals began to decompose at 70.2^{o} and the entire crystalline mass was opaque at 71.4^{o}.

Fig. 12. Cuprous chloride-2-butyne crystalline complex in the presence of mother liquor (well, x100).

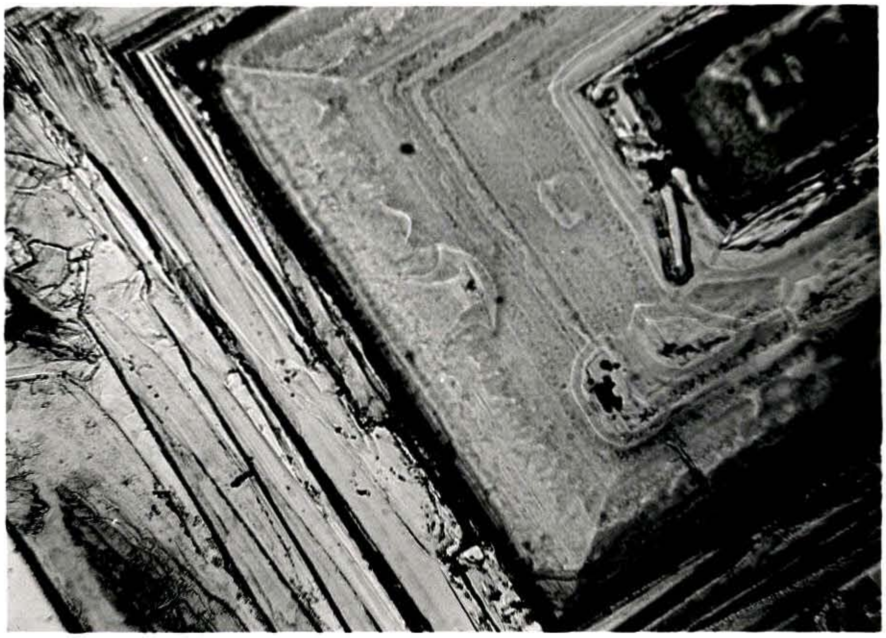

Fig. 13. The same cuprous chloride-2-butyne crystal as in Fig. 12 after 20 sec. decomposition time (well, x100).

System; Cuprous Bromide-2-Butyne. The crystalline complex of this system has been observed only in the acicular habit as indicated in Fig. 14. These needle like crystals extinguish between crossed Nicol prisms when the needle axis is parallel to the electric vector.

Decomposition of the cuprous bromide-2-butyne crystals takes place in the range 54.8-55.0° when "B" is at 25.0°. At 55.4° decomposition is nearly complete.

System; Cuprous Chloride-2-Pentyne. Solutions of cuprous chloride in 2-pentyne easily dissociate into the inorganic constituent and the alkyne without the formation of the crystalline complex. In sealed ampoules the crystalline complex is readily prepared from solution at 25° when the solution is alternately chilled at a low temperature and allowed to warm to room temperature until the crystalline complex is observed. Large poorly defined crystalline masses consisting of relatively few single crystals develop when the ampoule is allowed to remain at ambient temperatures for long periods of time. Fig. 15 shows part of a single crystal grown in an ampoule. The symmetry of the somewhat tabular crystal was that of Fig. 16. Columnar crystals, which extinguish between Nicol prisms parallel to their axis develop upon slow evaporation of the excess alkyne.

When the capillary end of the melting point apparatus is introduced into the melting point bath at 29° and when

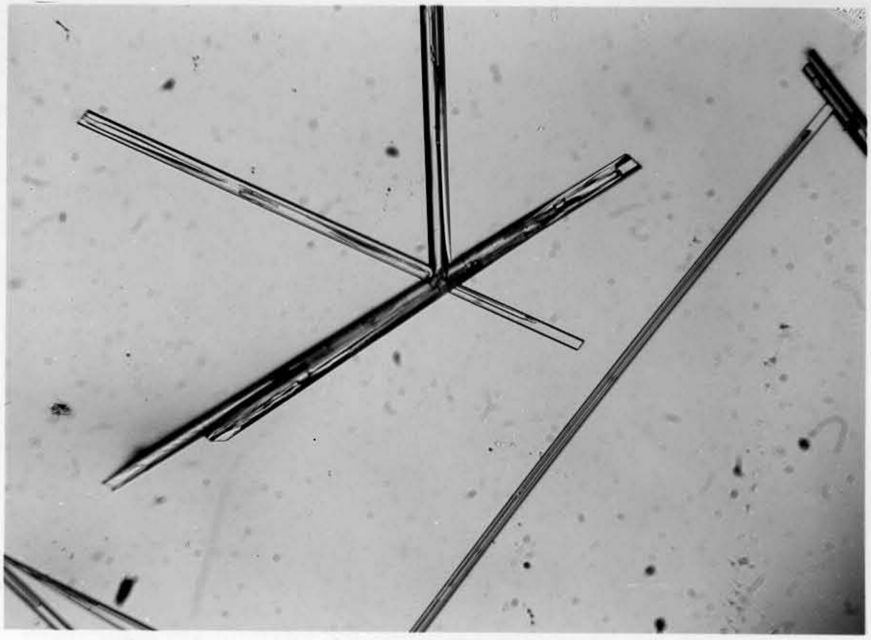

Fig. 14. Cuprous bromide-2-butyne crystalline complex in the presence of mother liquor (well, x100).

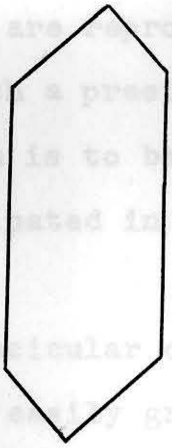

Fig. 16.

Fig. 15. Cuprous chloride-2-pentyne crystal, mother liquor (ampoule, x100).

bulb "B" is placed in the constant temperature bath at 25° and the temperature of the melting point bath slowly increased, the following is observed:

(i) a small part of the dry crystalline mass dissolves in alkyne condensed from the gaseous phase;

(ii) in the temperature range 33.8-35.6° the remaining crystalline complex melts or dissolves forming a colorless liquid in the capillary;

(iii) at 47° a white solid begins to precipitate from the solution;

(iv) the precipitate increases in its rate of development until 56.6° when the liquid begins to evaporate leaving behind a white solid on the capillary walls.

As in the rest of the melting point determinations with the apparatus in Fig. 2, the above phenomena are reproducible with the exception of the temperature at which a precipitate is first formed from solution. The exception is to be expected, however, as supersaturation may be anticipated in such situations.

<u>System; Cuprous Bromide 2-Pentyne</u>. The acicular crystals of the cuprous bromide-2-pentyne complex are easily grown in a manner similar to that described for the growth of the cuprous chloride-2-pentyne complex. These crystals extinguish between crossed Nicol prisms parallel to their needle axis. They are stable at room temperature.

When the bulb "B" is at 25° the dry crystalline complex

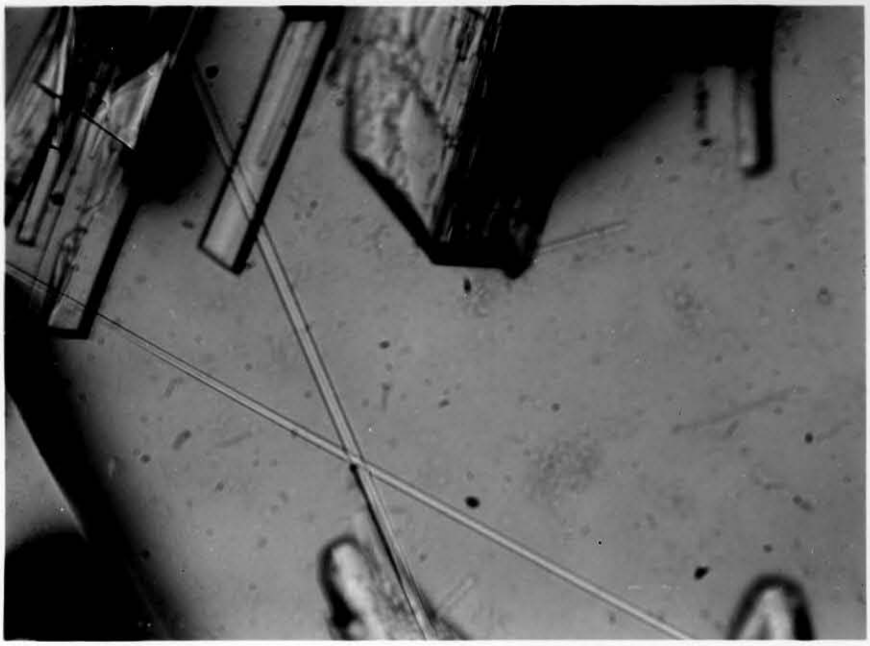

Fig. 17. Cuprous chloride-3-hexyne complex crystals, mother liquor (well, x100).

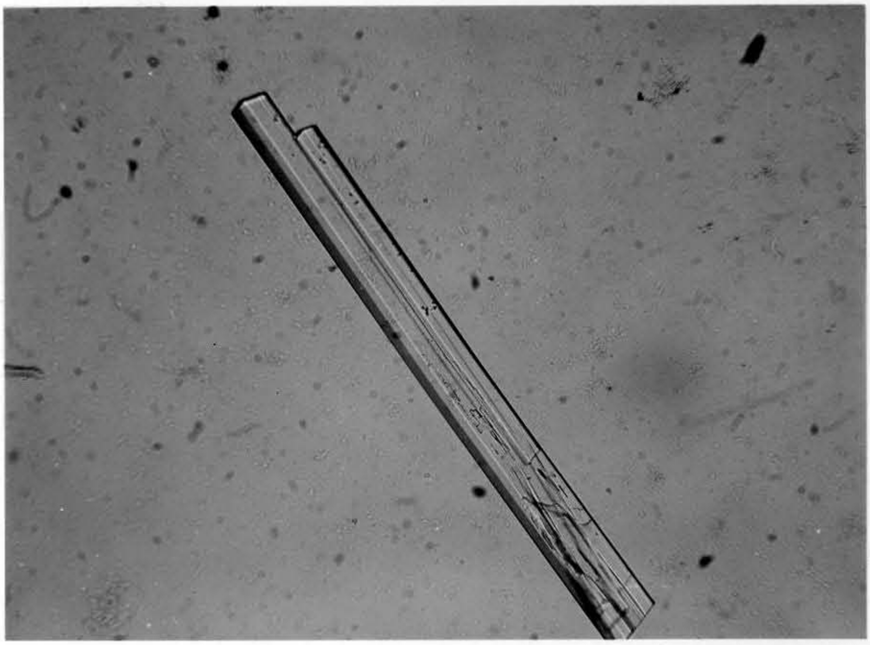

Fig. 18. Cuprous chloride-3-hexyne complex crystals, mother liquor (well, x100).

in the capillary at 25° begins to dissolve, at 27°, however, the excess alkyne distills off and at 35° only the dry crystalline mass remains. At 35.8° a subtile change is observed in the crystalline mass. This change, a darkening to a very light brown is followed at 44.5° by the obvious decomposition of the complex.

System; Cuprous Chloride 3-Hexyne. The crystalline complex of this system is easily grown from solution to form the extreme acicular crystals shown in Fig. 17. Upon standing in the presence of their mother liquor, the crystals develop a more columnar habit (Fig. 18) which extinguishes between crossed Nicol prisms parallel to the long axis.

When the vapor pressure of 3-hexyne above the crystals is decreased below a certain value, the crystalline complex often dissociates in isolated regions in contrast to the general areas of dissociation exhibited by the cuprous chloride-2-pentyne, cuprous bromide-2-pentyne, and cuprous bromide-2-butyne complexes and in contrast to the general areas usually but not always shown by the cuprous chloride-2-butyne complex (Fig. 13).

The nucleated dissociation of the cuprous chloride-3-hexyne complex is clearly illustrated in Fig. 19, 20, 21, 22, and 23. Fig. 19 shows a large single crystal in the presence of other crystalline masses and some mother liquor. The glass slide covering the well was removed and the excess alkyne allowed to evaporate. After 5 sec. the cover was

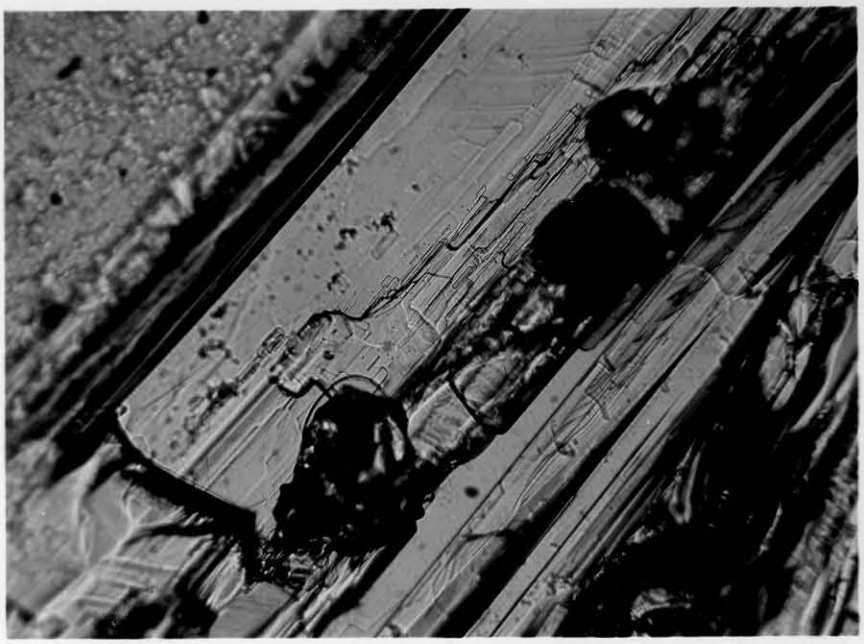

Fig. 19. Cuprous chloride-3-hexyne crystalline complex, some mother liquor (well, x100).

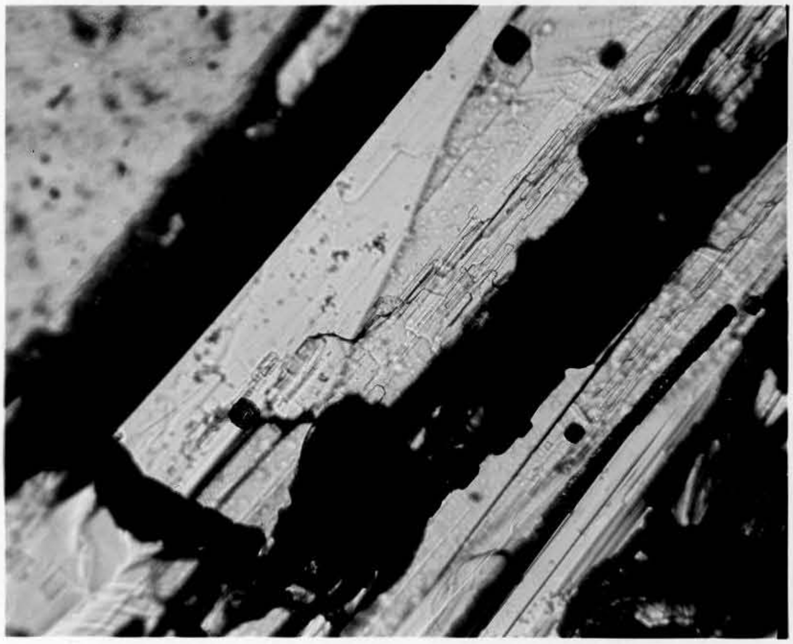

Fig. 20. Cuprous chloride-3-hexyne crystalline complex, no mother liquor, decomposition time, 5 sec. (well, x100).

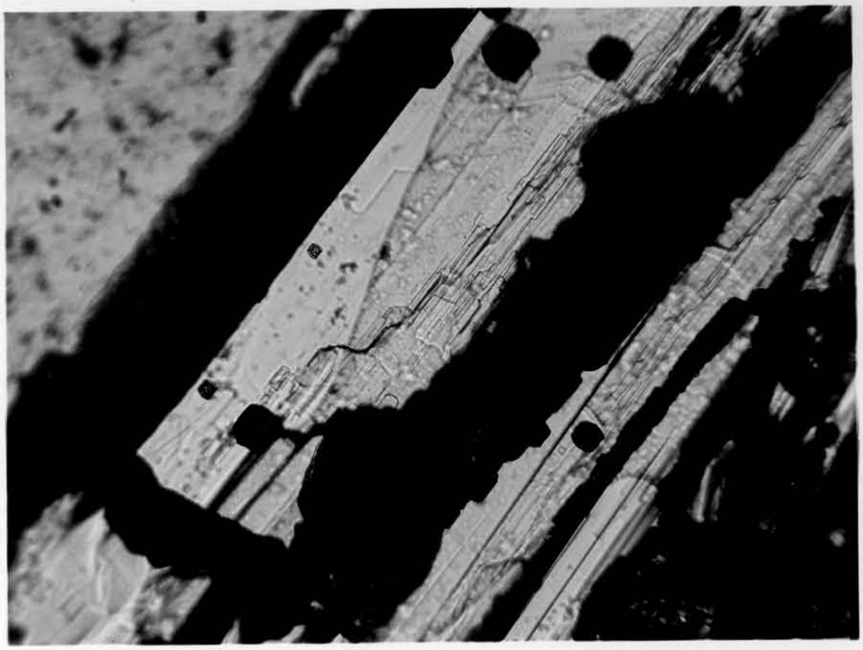

Fig. 21. Cuprous chloride-3-hexyne crystalline complex, decomposition time, 10 sec. (well, x100).

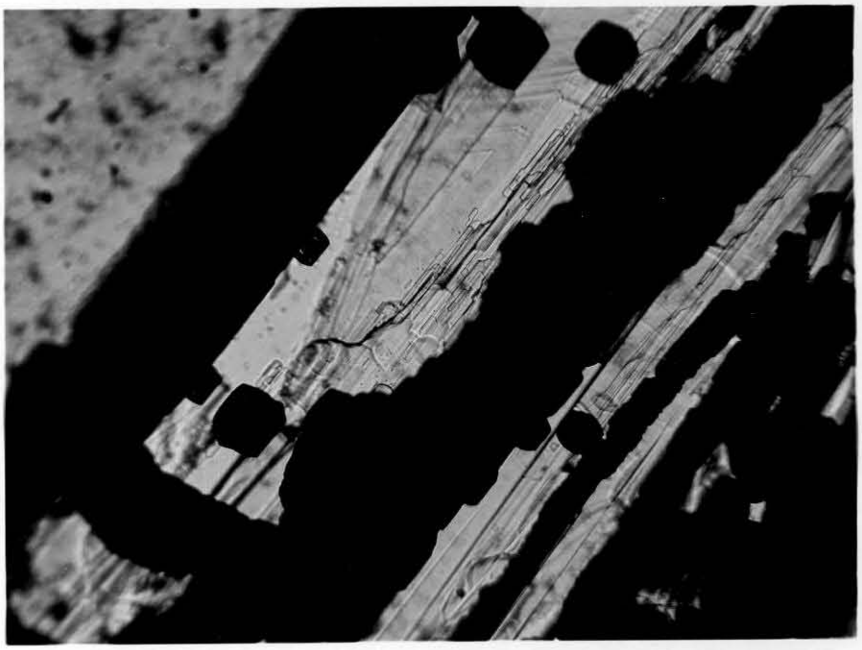

Fig. 22. Cuprous chloride-3-hexyne crystalline complex, decomposition time, 15 sec. (well, x100).

Fig. 23. Cuprous chloride-3-hexyne crystalline complex, decomposition time, 20 sec. (well, x100).

replaced and the photomicrograph Fig. 20 was taken. The total time the cover was off is designated as the "decomposition time". In Fig. 21 for example, the cover was removed twice for approximately 5 sec., hence the "decomposition time" was 10 sec.. The black deposit demarking the area of the nucleation shown in the photomicrographs is actually white opaque cuprous chloride. The symmetry (p 2) of the decomposition area is that of the crystalline face but this area is more symmetrical in its dimensions. Well defined nucleated decomposition for addition complexes of other systems has not been observed.

When the dry crystalline cuprous chloride-3-hexyne complex in the capillary of the melting point apparatus is introduced into the melting point bath at 28° and when "B" is at 25° the crystals start dissolving in alkyne condensed from the gaseous phase. At 40° the remaining crystalline mass begins to melt or dissolve rapidly and at 40.6° only liquid remains. Well formed crystals of cuprous chloride are precipitated from the solution at 48°.

System; Cuprous Bromide 3-Hexyne. As Fig. 24 and 25 show the crystals of the cuprous bromide-3-hexyne complex grown from solution are very similar to the chloride analogue. The acicular crystals of the cuprous bromide-3-hexyne complex are soft and may be bent in some case through large angles (30°) without sign or fracture. In ampoules long single crystals have been observed; one exceptional crystal measured 3.5 cm..

When bulb "B" is at 25° the dry cuprous bromide-3-hexyne crystalline complex decomposes when the melting point bath is at 44.3-44.4°. On a Kofler micro hot stage decomposition of a single crystal under a drop of glycerol occurred at 45°. This latter method, however, is tedious to standardize and is undependable.

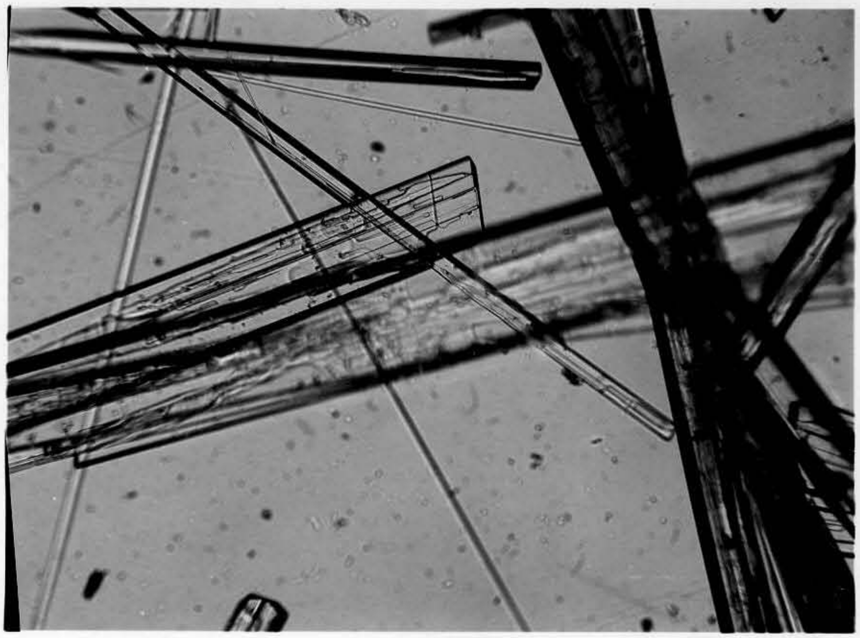

Fig. 24. Cuprous bromide-3-hexyne complex crystals, mother liquor (well, x100).

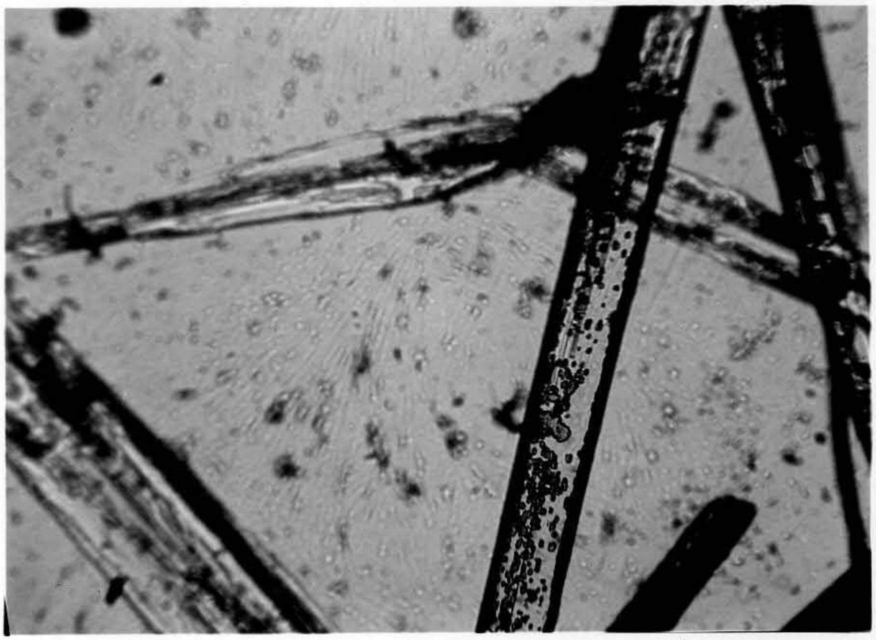

Fig. 25. Cuprous bromide-3-hexyne complex crystals, no mother liquor, decomposition time, 10 sec. (well, x100).

E. NOTATION.

The author will use the following notation in the thesis.

A	activity; coefficient of an equation
a	unit cell dimension
B	coefficient of an empirical equation
b	unit cell dimension
C	the ratio in the crystalline complex of the weight of ligand to the weight of cuprous halide; coefficient of an empirical equation
C'	integration constant
c	unit cell dimension
Cu_T	total weight of cuprous halide in a system
d_c	density of crystalline complex
$d_{c_{est.}}$	an estimated d_c
$d_{c_{M.V.}}$	a d_c calculated from the molecular volumes of the pure components assuming that they are additive
$d_{c_{soln.}}$	a d_c calculated from the composition and density of a solution
d_s	density of a saturated solution
E	extinction coefficient
h	partial molar enthalpy
$\Delta h_{Dis.}$	heat of dissociation of one mole of crystalline complex to gaseous ligand at pressure P_c and solid inorganic constituent
$\Delta h_{fus.}$	heat of fusion of one mole of solute
Δh_L	heat of dissociation of one mole of crystalline

	complex to the liquid ligand at one atmosphere and the solid inorganic constituent
Δh_R	heat of reaction for one mole of cuprous bromide-ligand complex plus one mole of cuprous chloride to form one mole of the chloride complex plus one mole of cuprous bromide
$\Delta h_{soln.}$	heat of solution of one mole of solute
$\Delta h_{vap.}$	heat of vaporization of one mole of ligand
$K_{Dis.}$	the dissociation constant
ℓ	path length of optical cell
n	the ratio of moles of ligand to moles of inorganic constituent in an isolated system
n'	the ratio of moles of ligand in the non-gaseous phases to moles of inorganic constituent present
N	a number indicating the 'average' amount of association of solute in solution ($N=2$ for a solute which is completely dimerized)
N/γ'	a rough measure of the degree of association of a solute, see N and γ'
P	a vapor pressure
ΔP	a pressure difference, either $P_o - P$ or $P_o - P_s$
P_c	a dissociation vapor pressure
P'_c	a pressure suspected to be P_c
$P_{c_{ex.}}$	an experimental P_c
$P_{c_{cal.}}$	a calculated P_c
P_d	the decomposition vapor pressure of a crystalline complex, defined by $P_d = P_o = P_c$

P'_d	the decomposition vapor pressure of a crystalline complex, defined by $P'_d = P_s = P_c$
$P_{in.}$	the initial pressure
P_o	the vapor pressure of the pure ligand
P_R	the pressure at which the dissociation vapor pressures of two complexes, in equilibrium with the same ligand but containing different inorganic constituent, are equal
P_s	the vapor pressure of a saturated solution
S	the ratio in the liquid phase of the weight of ligand to the weight of inorganic constituent
s	partial molar entropy
$\Delta s_{Dis.}$	entropy change corresponding to $\Delta h_{Dis.}$
Δs_L	entropy change corresponding to Δh_L
Δs_R	entropy change corresponding to Δh_R
T	absolute temperature
T_d	temperature corresponding to P_d
T'_d	temperature corresponding to P'_d
T_m	temperature at which P_s passes through a maximum
T_R	temperature corresponding to P_R
Un	alkyne, unsaturated hydrocarbon
Un_T	the total weight of alkyne in a system
v	partial molar volume
w_c	the total weight of the complex crystalline phase
w_T	the total weight of the complex crystalline phase and the liquid (ligand) phase
x	mole fraction

x_h	the mole fraction of the solvent
x_S	the mole fraction of the solute
α	a crystalline phase
β	a crystalline phase; angle between a and c in monoclinic unit cell
γ	activity coefficient
γ'	an artificial 'average' activity coefficient
φ_{Un}	the fugacity of an unsaturated compound
	molar free energy (chemical potential
$\Delta\mu_{Dis.}$	chemical potential change corresponding to $\Delta h_{Dis.}$
$\Delta\mu_L$	chemical potential change corresponding to Δh_L
$\Delta\mu_R$	chemical potential change corresponding to Δh_R
$\sum$	summation symbol
log	common logarithm
ln	natural logarithm
d	total differential
∂	partial differential,
Δ	symbol indicating excess of value of a function of a state in final over initial state

Superscripts denote: g, gaseous phase; l, liquid phase; s, solid phase; *, pure liquid phase.

Subscripts denote: c, crystalline complex; cal., calculated; ex., experimental; in., initial; h, solvent; max., optical properties associated with most intense absorption peak; S, solute; s, saturated solution; Un, unsaturated hydrocarbon (ligand).

F. VAPOR PRESSURE MEASUREMENTS OF THREE PURE ALKYNES.

The vapor pressure over the pure liquids, 2-butyne, 2-pentyne, and 3-hexyne, was determined as a function of temperature from 3° to 28° at intervals of approximately 1.5°.

Experimental Details. The vapor pressures of the three liquids were determined simultaneously in constant temperature bath No. 2, described on page 9. The reaction flask (type No. 1, page 23) had in each case been degassed and flamed out from time to time over a period of ten days. The liquid surfaces of the alkynes were broken by the vibrating action of the glass enclosed mites, actuated by the underwater magnetic stirrer, (see page 10) placed at the edge of the reaction flask. The inside diameter of the manometers joined to the reaction flasks were 14 - 16 mm.. The thermometer used with the bath could be read (with a telescope) with a precision of ±0.01°. The thermometer was calibrated in the temperature range mentioned above at fifteen places by comparison with a certified N.B.S. thermometer. Stem corrections were applied. In order to calculate the reduced pressure in mm. of Hg at 0° from the measured pressure it was assumed that the temperature of the mercury in the manometers was that of the thermometer (accurate to within ±0.1°) strapped to the outside of one of the columns of mercury. Each measurement was taken as the average of at least two readings.

In each case 10-12 ml. of alkyne was distilled into the equilibration flask for the vapor pressure measurements. After approximately 35 measurements were made, nearly 50 percent of the alkyne was distilled at 5.0 0.1° to a receiver cooled in an ice-water mixture. Then approximately 30 additional measurements were made.

The source of the alkynes used in these measurements were portions of purified samples from previously unopened containers supplied by Farchan Research Laboratories. All distillations were carried out as described on page 27, 2-butyne; page 28, 2-pentyne; or page 28, 3-hexyne.

2-Butyne. This alkyne (103 g.) was distilled through a 35-cm. Vigreux column from sodium. The second fraction of the distilled material (68 g.) was then transferred under nitrogen to a 40-cm. helix packed column and redistilled. The second fraction was again collected and transferred to a high vacuum apparatus under nitrogen. The physical constants for 2-butyne were; second fraction Vigreux column, b.p. 26.7°(746 mm.); $n^{25}D$ 1.3890: second fraction helix packed column, b.p. 26.8° (748 mm.); $n^{25}D$ 1.3890. The redistilled 2-butyne was then degassed, distilled once from a dry ice-acetone bath to a liquid nitrogen cooled receiver and treated three times with freshly cut sodium at reduced pressures for short periods of time (ca. 5 min.) at 0° in a manner described on page 27. No reaction with sodium was observed. Physical constants: $n^{25}D$ 1.3889;

d^{25} 0.6857 Lit.: b.p. 26.99°(760 mm.); $n^{25}D$ 1.3893; d^{25} 0.6856 (33): b.p. 26.97° (760 mm.); $n^{20}D$ 1.3918; d^{20} 0.6906 (34).

2-Pentyne. When eighty five grams of 2-pentyne were treated with freshly cut sodium under reduced pressure some action was observed to take place, but the residue after vacuum distillation of the 2-pentyne was practically negligible. The recovered alkyne was then distilled under nitrogen once through the 35-cm. Vigreux column and twice through the helix packed column. The physical characteristics of the successive second fractions were b.p. 55.1-55.3° (740 mm.); $n^{25}D$ 1.4004; 64 g.: b.p. 55.3-55.4(741 mm.); $n^{25}D$ 1.4005; 44 g.: b.p. 55.4 (742 mm.); $n^{25}D$ 1.4005. The purified 2-pentyne was transferred to the high vacuum apparatus and degassed, then it was distilled from dry ice-acetone bath to a liquid nitrogen cooled receiver. The collected alkyne showed the presence of a small amount of a filmy white solid at -78°. The distillation from the dry ice-acetone bath was repeated. The alkyne was then treated with freshly cut sodium five times in a manner like that described above for 2-butyne. Some reaction was observed to take place during the first two treatments. No indication of a solid at -78° was present after the final treatment with sodium. Physical constants; $n^{25}D$ 1.4005; d^{25} 0.7055. Lit: b.p. 56.07°(760 mm.); $n^{25}D$ 1.4009; d^{25} 0.7055 (33): b.p. 56.12(760 mm.); $n^{20}D$ 1.40336; d^{20} 0.71040(34).

3-Hexyne. This alkyne, as obtained from Farchan Research Laboratories, showed a slight amount of white solid at -78°. Ninety grams of the alkyne were distilled under nitrogen through the 35-cm. Vigreux column. The second fraction of this distillation was then redistilled through the Vigreux column under nitrogen and finally through the 40-cm. helix packed column. The physical characteristics of the successive collected fractions were b.p. 80.2-80.7°(748 mm.); $n^{25}D$ 1.4090; 78.5 g.: b.p. 80.6°(746 mm.); $n^{25}D$ 1.40895; 63 g.: b.p. 80.6° (747 mm.); $n^{25}D$ 1.4090. The last collected sample was transferred under nitrogen to the high vacuum apparatus and degassed. The purified 3-hexyne was then treated three times with freshly cut sodium but showed no reaction. At -78° no solid was present. The physical characteristics are: $n^{25}D$ 1.4090; d^{25} 0.7185. Lit: b.p. 81.43°; $n^{20}D$ 1.4112; d^{20} 0.7226 (34): b.p. 80.5-80.6°(746 mm.); $n^{25}D$ 1.4090; d^{25} 0.7185 (35).

The infrared spectra of the 3-alkynes were recorded in carbon tetrachloride in a 1-mm. sodium chloride cell at the following concentrations in weight percent: 2-butyne, 1.06; 2-pentyne, 1.86; 3-hexyne, 1.16.

Discussion of Results. The author hoped that by obtaining the vapor pressure data at small temperature intervals it would be possible to fit the data by the method of least squares to curves of the form of eq. 1, where A, B, and C $\not\leq 0$.

$$\log P_o = A/T + B \log T + C \qquad (1)$$

If the data could be reduced to the form of eq. 1 then some confidence in an extrapolated value of $P_{o\,cal.}$ would be justified. The solution of the normal equations yields (in the case of each alkyne) a determinant which is very near to zero; this indicates that the normal equations are not independent, (i.e. that A, B, or C should be equated to zero).

Accordingly the vapor pressure data were fitted to curves of the form eq. 2. The results for each alkyne

$$\log P_o = A/T + C \qquad (2)$$

will be discussed separately.

2-Butyne. The work of G.B. Heisig and H.M. Davis (36) on the vapor pressure of 2-butyne can be favorably compared with the data presented here. They determined the vapor pressure from -32° to 25° at intervals of approximately 5° and fitted (in a manner unstated) their data to a curve of the form eq. 1. Their constants A, B, and C are summarized in Table 6 with the constants A and C of the three alkynes investigated here; the mean deviation and the maximum deviation and its associated temperature are also given. When the mean deviation of the author's experimental values

Table 6

Empirical Constants for Determination of $P_{o_{cal.}}$

Alkyne	A	σ(A)	B	C	σ(C)	Mean deviation mm.	Max. deviation mm.	Temp. of max. dev. °C.
2-Butyne	-1458.92	0.04	0	7.7431	0.0042	0.8	2.9	26.3
2-Butyne#	-2047.473		-4.8153	21.6295		0.6	2.4	20.0
2-Pentyne[t]	-1668.37	0.12	0	7.969	0.013	0.8	2.0	26.3
2-Pentyne[b]	-1664.31	0.07	0	7.957	0.006	0.3	0.7	23.2
2-Pentyne[a]	-1670.49	0.07	0	7.974	0.008	0.4	1.1	21.3
3-Hexyne	-1867.4	0.4	0	7.193	0.014	0.25	1.2	21.3

σ is the standard deviation of the constants A and C.

\# G.B. Heisig and H.M. Davis (36).

[t] All the vapor pressure data for 2-pentyne.

[b] 2-Pentyne data before fractionation.

[a] 2-Pentyne data after fractionation.

$$\log P_{o_{cal.}} = A/T + B \log T + C$$

from the empirical curve given by G. B. Heisig and Davis for 2-butyne was calculated it was found to be 1.2 mm., which is less than the sum (1.4 mm.) of the mean deviation of the two independent studies. The present study can be visually compared with the work of the previous investigators in Fig. 26. In Table 7 where the experimental vapor pressure, $P_{o_{ex.}}$ is compared with the value $P_{o_{cal.}}$ calculated from the equation obtained by the method of least squares it can be pointed out that in every measurement where $P_{o_{cal.}} >$ $P_{o_{ex.}}$ the temperature is either greater than 21.26° or less than 6.06°. In all other cases $P_{o_{ex.}}$ is greater than $P_{o_{cal.}}$. This observation leads one to believe that if a term of the form B log T was introduced, the mean deviation (0.8 mm.) might be substantially reduced. The heat of vaporization for 2-butyne as calculated from A (eq. 2, Table 6) determined in the present study is $\Delta h_{vap.} = 6.67$ Kcal/mole . The A term in the equation given by Heisig and Davis does not give a suitable value (9.38 Kcal/mole) for comparison. However, when the values as calculated from the curve given by the above mentioned authors was fitted between 3° and 28° by the methods of least squares to a curve of the form of eq. 2 then the heat of vaporization was found to be 6.68 Kcal/mole . The boiling point at 760 mm. calculated with eq. 2 from the present data is 26.93°. No appreciable effect of fractionation was observed when 50 percent of the alkyne was distilled from the equilibration flask.

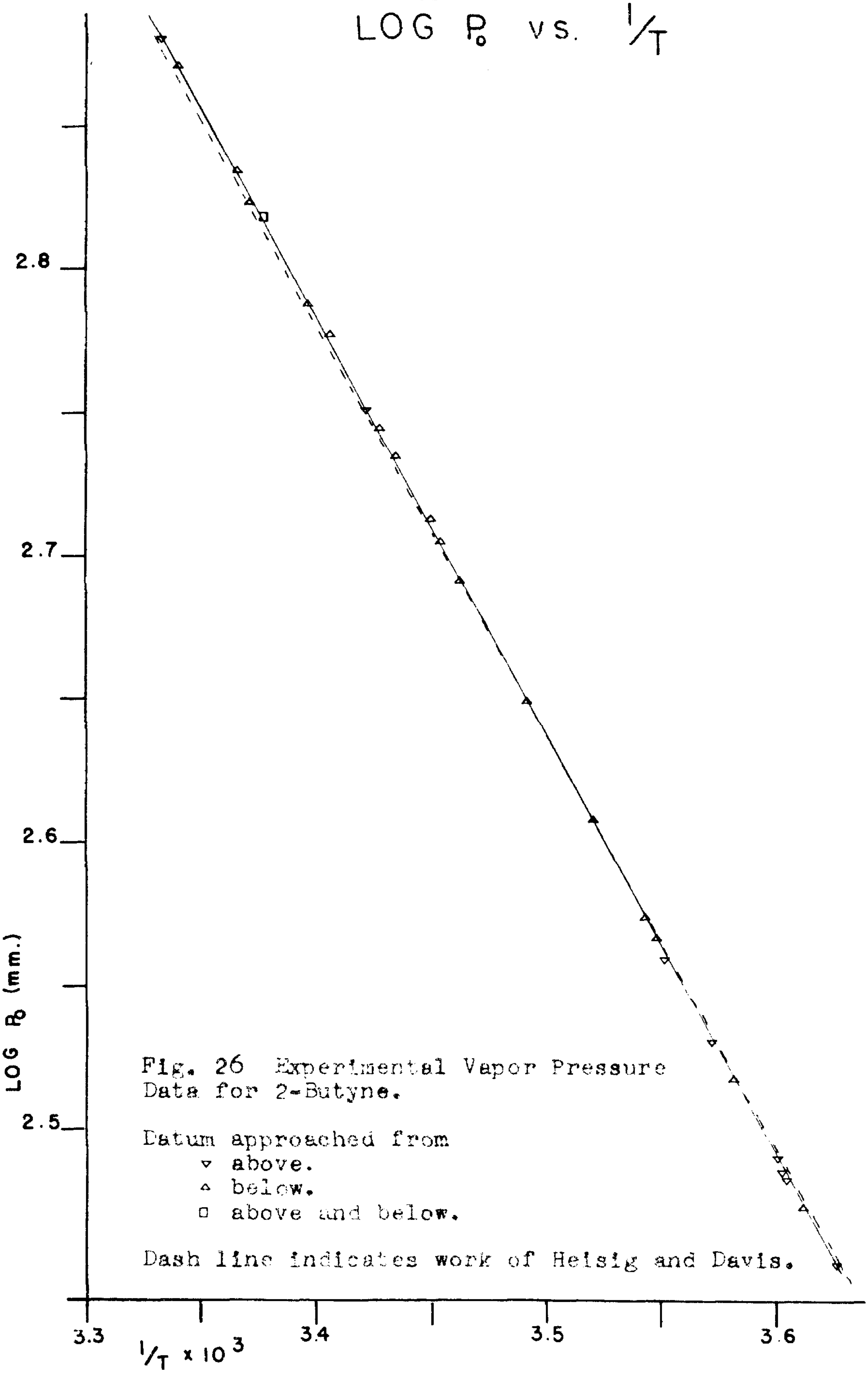

Fig. 26 Experimental Vapor Pressure Data for 2-Butyne.

2-Pentyne. In contrast to the above case 2-pentyne showed definite fractionation when about half of the alkyne was distilled from the equilibration flask. This was evident when a least squares treatment of all the data gave $P_{cal.} < P^{b}_{ex.}$ and $P_{cal.} > P^{a}_{ex.}$ where the superscripts b and a denote, respectively, before distillation and after distillation. The mean deviation of the vapor pressure from the calculated curve was 0.8 mm.. This could be reduced to 0.3^{b} mm. and 0.4^{a} mm. if the data were treated as two groups, i.e. $P^{b}_{ex.}$ and $P^{a}_{ex.}$. Data for comparing $P_{ex.}$ with $P_{cal.}$ for 2-pentyne is correspondingly divided into two sections. Tables 8 and 9, Fig. 27, demonstrates the clear delineation of the data into these groups. The heat of vaporization and the extrapolated boiling points for these two curves are $\Delta h^{b}_{vap.} = 7.61$ Kcal/mole , 54.70° and $\Delta h^{a}_{vap.} = 7.64$ Kcal/mole , 54.0°. This can be compared with 57.12° as given by N.B.S. (34) as the boiling point of 2-pentyne. When the remaining distillate was frozen at the end of the vapor pressure measurements a white filmy solid was apparent. The elapsed time between the final purification of the alkyne and the distillation that resulted in fractionation was 35 days. It is not known if the alkyne which was purified was a constant boiling mixture or if rearrangement gave rise to a different unsaturated hydrocarbon. Rearrangement of alkynes under storage conditions is well known. 2-Butyne demonstrated fractionation

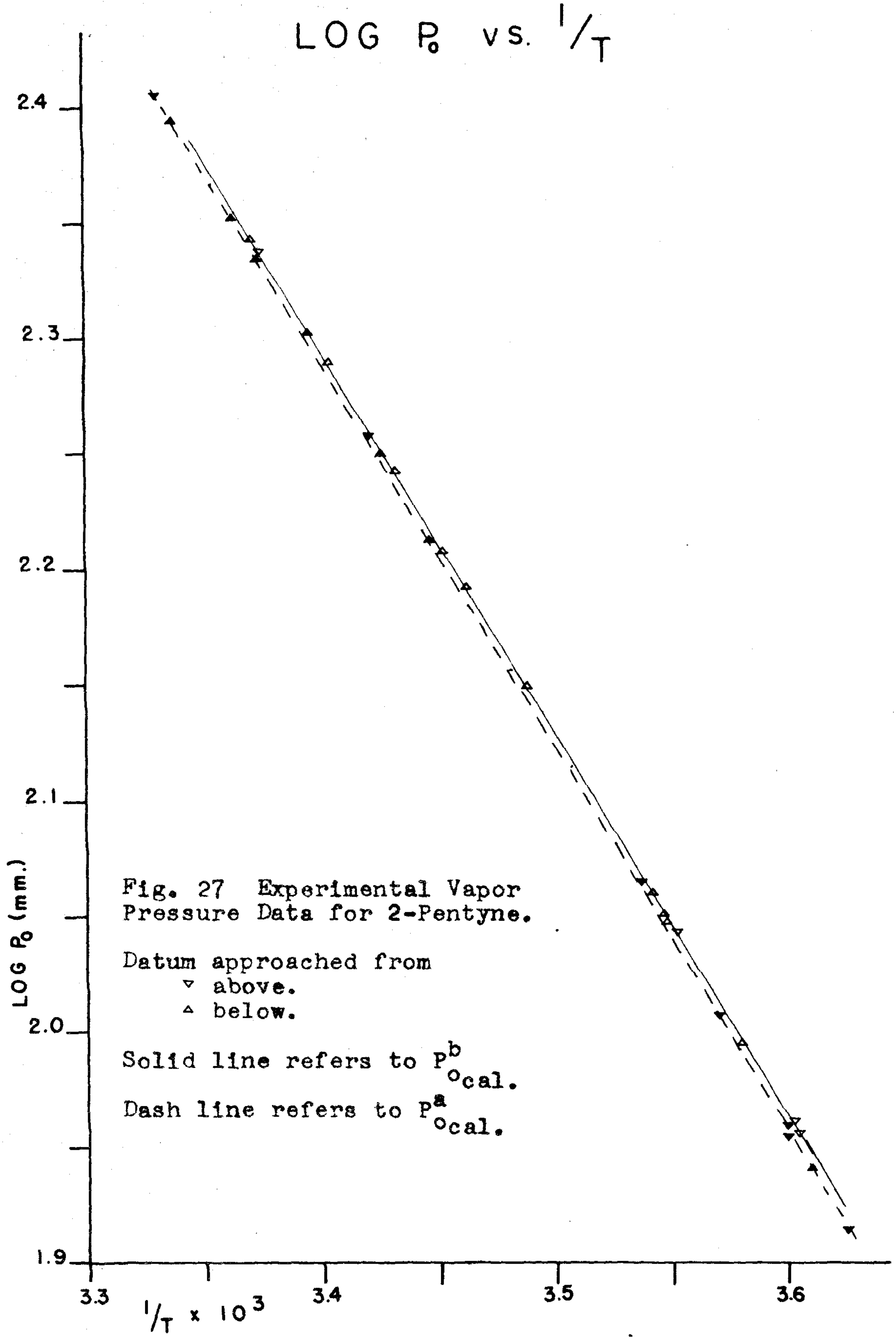

Fig. 27 Experimental Vapor Pressure Data for 2-Pentyne.

Datum approached from
▿ above.
▵ below.

Solid line refers to $P^b_{o\,cal.}$

Dash line refers to $P^a_{o\,cal.}$

upon distillation after nine months in storage (in contact with mercury). The equation which will be assumed correct for the purposes of this thesis will be that which describes P^{b}_{o} as a function of temperature.

3-Hexyne. Upon removal of about one-half of the total 3-hexyne by distillation, fractionation did not occur to any appreciable extent. In fact $P^{a}_{o_{ex.}}$ was greater than $P^{b}_{o_{cal.}}$ on the average to the extent of about 0.1 mm.; although the direction of this deviation was persistent it was well within the maximum expected error of 0.4 mm.. The average deviation (0.25 mm.) of the experimental values from the calculated values indicate that the expected error may be 0.1 mm. too large. The heat of vaporization and the extrapolated boiling point were calculated to be 8.54 Kcal/mole and 78.3° respectively. Deviations of the extrapolated $P_{o_{cal.}}$ from the observed values of Bried and Hennion (37) were large, for example 846 and 744 mm. at 81.50°, 664 and 600 mm. at 74.5°, and 260 and 244 mm. at 50°. These deviations are doubtless due in large measure to the neglect of heat capacity effects and should, therefore, be expected. The heat of vaporization of 3-hexyne as calculated from the data of Bried and Hennion is corresponding somewhat lower (*i.e.*, *ca.* 82 Kcal/mole). The experimental data are listed in Table 10 and compared with the vapor pressures as calculated from the least squares treatment.

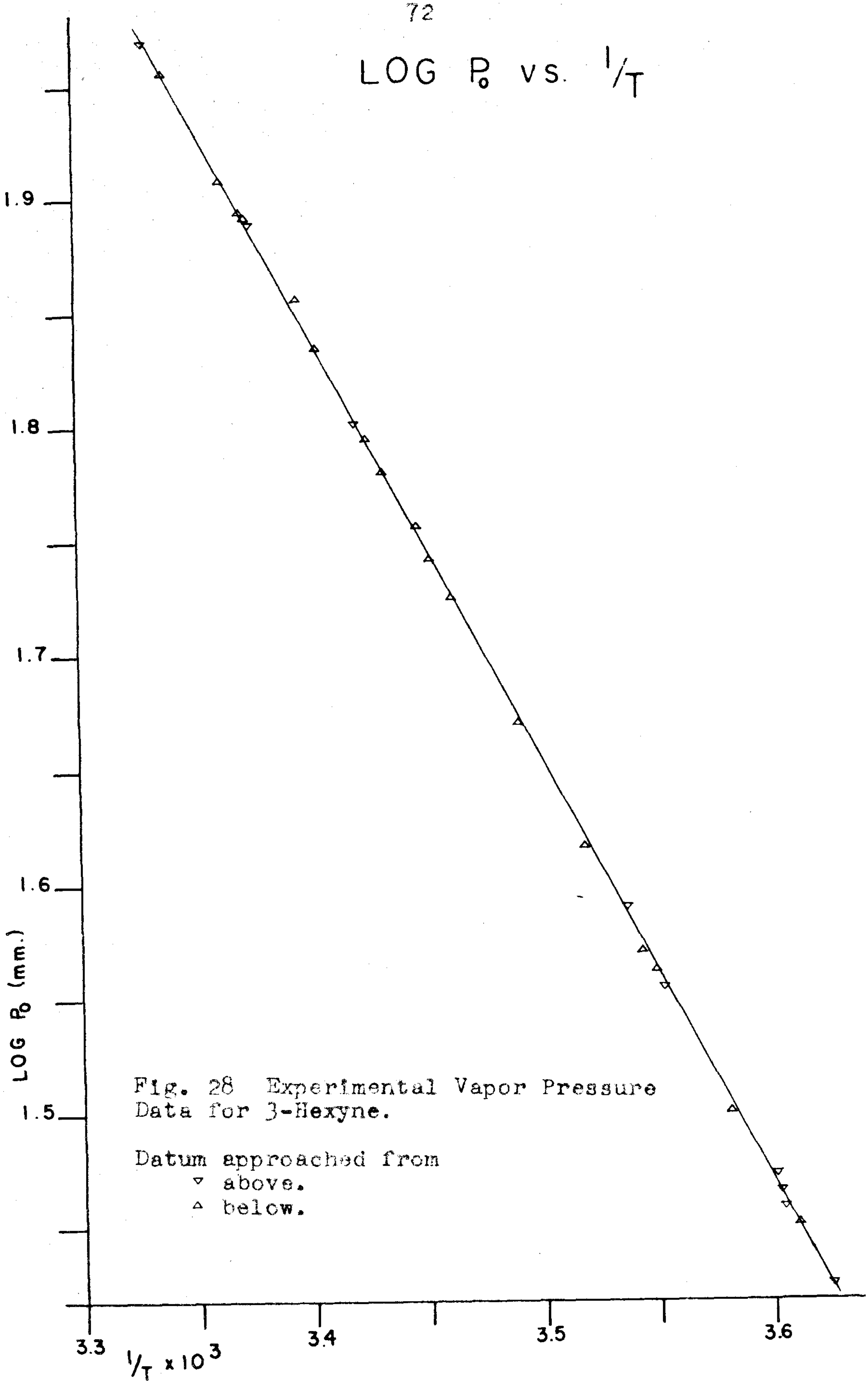

Fig. 28 Experimental Vapor Pressure Data for 3-Hexyne.

Datum approached from
▽ above.
△ below.

Two sources of Error. Possible sources of error not as yet described are the two following:

(i) Room temperature changes were often as much as 8° in an hour's time. It might well be expected that the temperature of the mercury column in the manometers lagged considerably behind room temperature. This would introduce a small error in the correction of the pressure to mm. of Hg at 0°.

(ii) Disturbances observed in other experiments indicated that the bath temperatures may not be constant due to temporary large changes of temperature in the cooling water. Consequently even though the bath temperatures as measured were correct the listed hours of equilibration in Tables 7, 8, 9, and 10 may be much greater than was the actual case in some experiments.

Table 7

Vapor Pressure of 2-Butyne.

Ex.	Equilibration time hrs.	T °C.	$P^o_{ex.}$ mm.	$P^o_{cal.}$ mm.	Approach[a]
2	24	8.60	369.2	368.0	B
4	8	8.28	363.2	362.9	A
5	16	8.27	363.5	362.7	C
7	8	4.39	306.7	307.0	A
8	15	4.31	305.3	305.9	A
9	17	4.30	305.3	305.7	C
10	24	4.31	304.6	305.9	C
12	11.3	6.06	329.8	330.1	B
13	10.7	9.06	375.8	375.0	B
14	12.3	9.08	376.0	375.4	C
15	7.3	10.96	406.6	406.1	B
16	10.5	10.96	406.3	406.1	C
17	13.2	10.95	406.4	406.0	C
19	11	13.29	447.2	447.0	B
20	23	13.29	447.2	447.0	C
21	3.7	15.57	492.0	490.5	B
22	26.7	15.57	491.8	491.5	C
23	17.0	16.36	506.7	506.2	B
24	22.0	16.36	506.6	506.2	C
25	24.7	16.36	506.6	506.2	C
26	9	18.07	543.8	541.9	B
27	16	18.08	543.8	542.1	C
28	17.3	18.07	543.6	541.9	C
29	8.3	20.51	597.7	596.4	B
30	10.1	20.53	597.5	597.0	C
31	11.1	20.55	597.8	596.6	C
32	24.2	20.54	597.6	596.8	C
33	27.1	20.54	597.5	596.8	C
34	27	23.37	666.1	666.1	B
35	52	23.41	665.9	666.9	C
36	35	23.12	659.1	659.6	A
37	39	23.13	658.5	660.0	C
38	63	23.15	659.1	660.5	C
39	84	23.14	659.1	660.3	C
40	24	23.18	659.9	661.1	B
41	28	23.13	658.6	660.0	C
42	23	26.31	741.7	744.4	B
43	25.5	26.31	741.5	744.4	C
46	6	26.96	760.0	762.6	A
47	7.5	26.95	760.1	762.4	C
48	11	19.07	563.8	563.8	A
49	13	19.07	563.9	563.8	C

Table 7

Vapor Pressure of 2-Butyne.

(continuation).

Ex.	Equilibration time hrs.	T °C.	$P_{o_{ex.}}$ mm.	$P_{o_{cal.}}$ mm.	Approach[a]
52	25.6	18.60	554.7	553.5	B
53	4	24.08	682.7	684.2	B
54	12.0	6.79	340.8	340.5	A
56	36	9.49	382.7	381.9	A
57	54	9.49	382.8	381.8	C
58	6	4.63	309.6	310.2	A
59	24	4.63	310.2	310.2	C
60	28	4.65	309.1	310.9	C
61	30	4.64	310.0	310.6	C
62	24	2.65	283.8	284.4	A
63	38	2.63	283.6	284.2	C
64	12	3.77	298.3	298.7	B
65	76	3.79	298.7	299.0	C
66	18.5	3.76	298.4	298.6	C
67	17.0	16.81	516.1	515.5	B
68	28	16.84	516.2	516.2	C
69	32	16.83	516.1	515.8	C
70	24	21.26	614.0	614.1	B
71	28	21.29	614.5	614.9	C

[a] In this column A (above) means approach from a higher temperature, B (below) means approach from a lower temperature, and C means the temperature was constant.

Table 8

Vapor Pressure of 2-Pentyne.

(before fractionation).

Ex.	Equilibration time hrs.	T °C.	P_o ex. mm.	P_o cal. mm.	Approach[a]
1	22	8.56	111.7	112.1	B
2	24	8.60	112.7	112.4	B
4	8	8.28	110.5	110.6	A
5	16	8.27	110.6	110.5	C
7	8	4.39	91.3	91.4	A
8	15	4.31	90.7	91.0	A
9	17	4.30	91.1	90.9	C
10	24	4.31	90.8	91.0	C
12	11.3	6.06	99.2	99.2	B
13	10.7	9.06	114.9	114.8	B
14	12.3	9.08	115.0	114.9	C
15	7.3	10.96	124.8	125.7	B
16	10.5	10.96	125.8	125.7	C
17	13.2	10.95	125.7	125.5	C
19	11	13.29	140.4	140.3	B
20	23	13.29	140.4	140.3	C
21	3.7	15.57	156.2	155.9	B
22	26.7	15.57	156.2	155.9	C
23	17.0	16.36	161.7	161.6	B
24	22	16.36	161.6	161.6	C
25	24.7	16.36	161.9	161.6	C
26	9	18.07	175.0	174.7	B
27	16	18.08	175.2	174.8	C
28	17.3	18.07	175.2	174.7	C
29	8.3	20.51	195.2	194.9	B
30	10.1	20.53	195.3	195.1	C
31	11.1	20.55	195.2	195.0	C
32	24.2	20.54	195.4	195.0	C
33	27.1	20.54	195.3	195.0	C
34	27	23.37	220.8	221.1	B
35	52	23.41	220.8	221.4	C
36	35	23.12	218.2	218.6	A
37	39	23.13	218.3	218.8	C
38	63	23.15	218.2	218.9	C
39	84	23.14	218.2	218.9	C

[a] In this column A (above) means approach from a higher temperature, B (below) means approach from a lower temperature, and C means the temperature was constant.

Table 9

Vapor Pressure of 2-Pentyne.

(after fractionation).

Ex.	Equilibration time hrs.	T °C.	$P_{o\,ex.}$ mm.	$P_{o\,cal.}$ mm.	Approach[a]
40	24	23.18	217.0	217.3	B
41	28	23.13	216.4	216.9	C
42	23	26.31	248.1	248.9	B
43	25.5	26.31	248.1	248.9	C
46	6	26.96	255.3	255.9	A
47	7.5	26.95	255.2	255.8	C
48	11	19.07	181.5	181.1	A
49	13	19.07	181.4	181.1	C
51	23	18.59	177.9	177.2	B
52	25.6	18.60	177.9	177.3	C
53	4	24.08	225.4	226.0	B
54	12	6.79	101.7	101.7	A
56	36	9.49	116.4	115.9	A
57	54	9.49	116.9	115.9	C
58	6	4.63	90.4	91.3	A
59	24	4.63	91.4	91.4	C
60	28	4.65	91.4	91.4	C
61	30	4.64	91.5	91.5	C
62	24	2.65	82.5	82.7	A
73	38	2.63	82.6	82.6	C
64	12	3.77	87.5	87.5	B
65	16	3.79	87.6	87.6	C
66	18.5	3.76	87.5	87.5	C
67	17.0	16.81	163.6	163.4	B
68	28.0	16.84	163.8	163.7	C
69	32	16.83	163.8	163.5	C
70	24	21.26	200.8	199.7	B
71	28	21.29	200.2	200.0	C

[a] In this column A (above) means approach from a higher temperature, B (below) means approach from a lower temperature, and C means the temperature was constant.

Table 10

Vapor Pressure of 3-Hexyne.

Ex.	Equilibration time hrs.	T °C.	$P_{o_{ex.}}$ mm.	$P_{o_{cal.}}$ mm.	Approach[a]
1	22	8.56	36.6	36.7	B
2	24	8.60	36.8	36.8	B
4	8	8.28	39.9	40.2	A
5	16	8.27	36.1	36.2	C
7	8	4.39	29.2	29.2	A
8	15	4.31	28.7	29.1	A
9	17	4.30	28.8	29.1	C
10	24	4.31	28.7	29.1	C
12	11.3	6.06	31.7	32.0	B
13	10.7	9.06	37.3	37.7	B
14	12.3	9.08	37.6	37.8	C
15	1.3	10.96	41.5	41.8	B
16	10.5	10.96	41.5	41.8	C
17	13.2	10.95	41.5	41.8	C
19	11	13.29	47.0	47.3	B
20	23	13.29	47.0	47.3	C
21	37	15.57	53.3	53.2	B
22	26.7	15.57	53.3	53.2	C
23	17.0	16.36	53.3	55.4	B
24	22.0	16.36	55.2	55.4	C
25	24.7	16.36	55.3	55.4	C
26	9	18.07	60.5	60.5	B
27	16	18.08	60.6	60.5	C
28	17.3	18.07	60.6	60.5	C
29	8.3	20.51	68.4	68.3	B
30	10.1	20.53	68.4	68.4	C
31	11.1	20.55	68.3	68.4	C
32	24.2	20.54	68.5	68.4	C
33	27.1	20.54	68.5	68.4	C
34	27	23.37	78.6	78.7	B
35	52	23.41	78.6	78.9	C
36	35	23.12	77.6	77.7	A
37	39	23.13	77.7	77.8	C
38	63	23.15	77.6	77.9	C
39	84	23.14	77.7	77.8	C
40	24	23.18	77.7	78.0	B
41	28	23.13	77.7	77.8	C
42	23	26.31	90.4	90.8	B
43	25.5	26.31	90.4	90.8	C
46	6	26.96	93.2	93.6	A
47	7.5	26.95	93.2	93.6	C
48	11	19.07	63.5	63.6	A
49	13	19.07	63.6	63.6	C
51	23	18.59	62.4	62.1	B

Table 10

Vapor Pressure of 3-Hexyne.

(continuation).

Ex.	Equilibration time hrs.	T °C.	P_o ex. mm.	P_o cal. mm.	Approach[a]
52	25.6	18.60	62.3	62.1	C
53	4	24.08	81.2	81.5	B
56	36	9.49	39.0	38.6	A
57	54	9.49	39.1	38.7	C
58	6	4.63	29.8	29.6	A
59	24	4.63	29.8	29.6	C
60	28	4.65	29.9	29.6	C
61	30	4.64	29.9	29.7	C
62	24	2.65	26.6	26.5	A
63	38	2.63	26.7	26.5	C
64	12	3.77	28.3	28.2	B
65	76	3.79	28.3	28.3	C
66	18.5	3.76	28.3	28.2	C
67	17	16.81	57.5	56.7	B
68	28	16.84	57.4	56.8	C
69	32	16.83	57.6	56.8	C
70	24	21.26	72.1	70.9	B
71	28	21.29	72.0	71.1	C

[a] In this column A (above) means approach from a higher temperature, B (below) means approach from a lower temperature, and C means the temperature was constant.

G. COMPOSITION OF MOLECULAR ADDITION COMPOUNDS.

For a correct analysis of a molecular addition complex no component should be in excess. This condition may be a difficult one to achieve in the case of a molecular complex which is easily decomposed at the temperature of interest (6, 12, and 13). A study of the absorption rate of 3-hexyne by cuprous chloride near equal molar amounts of the two components indicated that an absorption method of analysis would be inconvenient (see page 113).

Theoretical. Let P be the vapor pressure of alkyne in contact (but not necessarily in equilibrium) with a cuprous halide-alkyne crystalline complex, let P_s be the equilibrium vapor pressure of alkyne over a solution saturated with cuprous halide complex, and let P_c be the equilibrium dissociation vapor pressure in contact with the system: cuprous halide, cuprous halide-alkyne complex. If P is less than P_c the complex will decompose into its components. Such decomposition is very rapid in the known cases of cuprous halide-alkyne crystalline complexes (see pages 45 and 49). Alternately, if P is greater than P_s then the crystalline complex may dissolve in the excess alkyne. This phenomenon also occurs with ease in the known cases of cuprous halide-alkyne solid complexes. If however $P_s \geq P \geq P_c$ and equilibrium is allowed to occur it may be expected that neither free cuprous halide nor solution will be present with the crystals of molecular complex.

Experimental *Methods*. With the above simple concept in mind the author attempted to prepare various samples of crystalline complexes for analysis. Three different methods will be described:

(i) To one end of a medium 10-mm. diameter sealing tube was attached via a section of constricted pyrex tubing a vacuum stopcock, to which was joined the male member of a standard taper 10/30 joint. At the other end of the sealing tube was a short section of 6-mm. tubing. Through this section of tubing was introduced 0.5 g. cuprous bromide. The tubing was freed of cuprous bromide particles and was removed with a gas-oxygen flame. When the seal was cool the vessel was evacuated and 4 ml. of 3-hexyne was condensed onto the cuprous bromide by high vacuum techniques. The stopcock was then closed and the vessel removed from the high vacuum apparatus. The vessel was then gently swirled until all the cuprous bromide had reacted. No solution was allowed to come in contact with either the sintered disk or the stopcock grease. The vessel was attached to the rough vacuum distillation stand whose essential parts for this experiment were in the order: vacuum line, cartesian diver pressure regulator (page 25), dry ice-acetone condenser, and pump. Excess 3-hexyne was removed from the cooled vessel (ice-bath) at a pressure which was slowly decreased until $P=78.0$ 0.5 mm.; *i.e.* 5 mm. below P_s at 25° (see Table 29). Drying at this pressure was continued for five minutes with the ice-bath removed. At the end of this time a microscopic examination indicated that some decomposition had taken place. In a second trial the drying, after the ice bath was removed, was shortened to three minutes, however, the results were still unfavorable.

(ii) In bulb "A" of a tared apparatus similar to that of Fig. 3 was placed 2.55 g. of cuprous chloride, then approximately 2 g. of 2-butyne was distilled into bulb "B". The tubing was then closed as indicated in Fig. 3 and the joint removed. Taking care that no cuprous chloride was removed from bulb "A", 2-butyne was allowed to react with the cuprous salt to form the solid adduct and solution.

Now it is clear that the solid complex can be freed from excess alkyne by lowering the temperature at bulb "B" in such a manner that $P_s \geq P \geq P_c$. This was accomplished by placing "A" in a Dewar containing acetone at 14° and "B" in a Dewar with acetone at 0°. In order to remove "B" from "A" and prevent charring during the sealing operation the temperatures of the bath were stepwise lowered 10° at a time to -78° by the changing of Dewars. The temperature of bulb "A" was always lowered first. After sealing and the removal of "B", bulb "A" was allowed to warm to room temperature; it was observed that some of the complex had decomposed. The weight of 2-butyne in bulb "A" was 1.27 g.. The molar ratio of 2-butyne to cuprous chloride was then 0.908 ± 0.005.

In the case of a previous unweighed trial, decomposition of the cuprous chloride-2-butyne complex did not occur until two days later. In this case decomposition was not general (as in Fig. 13) but occurred in isolated areas, similar to the series of pictures indicating the decomposition of the cuprous chloride-3-hexyne complex.

(iii) In view of the results of the attempts to prepare suitable samples for analysis described above it was decided that an analysis could most conveniently be completed in the following manner:

By means of a funnel placed in the barrel cuprous halide was introduced into the tared reaction flask "A" (see Fig. 29). The apparatus was then weighed in order to determine the amount of cuprous halide added. The plug was carefully greased (excess avoided) and positioned; then the vessel was evacuated for one hour. After the evacuated vessel containing the cuprous chloride was cleaned and reweighed by high vacuum technique 6-8 ml. of the alkyne under investigation was condensed into the reaction vessel.

Solution of the cuprous halide in the alkyne was accomplished with the aid of the "Boerner" shaker and, upon occasion, gentle warming. In the cases where the organic phase had a low vapor pressure, eg. 80 mm., a small section of rubber tubing was placed over the male member of the standard taper joint on the reaction vessel and a partial vacuum drawn. A screw clamp was used to maintain the vacuum.

This simple technique was of considerable aid in the prevention of leaks during the hours of shaking. Excess alkyne was removed according to the method described above (ii) using however the apparatus of Fig. 29. When possible the reaction vessel was kept at room temperature and the collecting bulb at 0°. When temperatures other than these were used both baths were stirred. The critical part of the determination and unfortunately the most suspect part was the microscopic examination of the reaction vessel after a suitable drying period. The microscope used was ten power. The solid molecular complex was considered wet if;

(i) drops of liquid were apparent on the sides of the container or in the crystalline interstices, and,

(ii) if the crystalline mass had a semi-transparent, somewhat dull appearance in one or more regions.

The solid molecular complex was considered dry:

(i) if no evidence of a liquid was apparent; and

(ii) if the crystalline mass had a bright white opaque appearance in all of its parts (except when single crystals were apparent).

The solid complex was considered decomposed if the cuprous halide was in evidence or if any single transparent crystal showed a white film or an opaque spot on it. A cuprous halide is differentiated from its molecular complex by its smaller size and the different shape of its crystals. Furthermore it is indicated by a dull white (cuprous chloride)

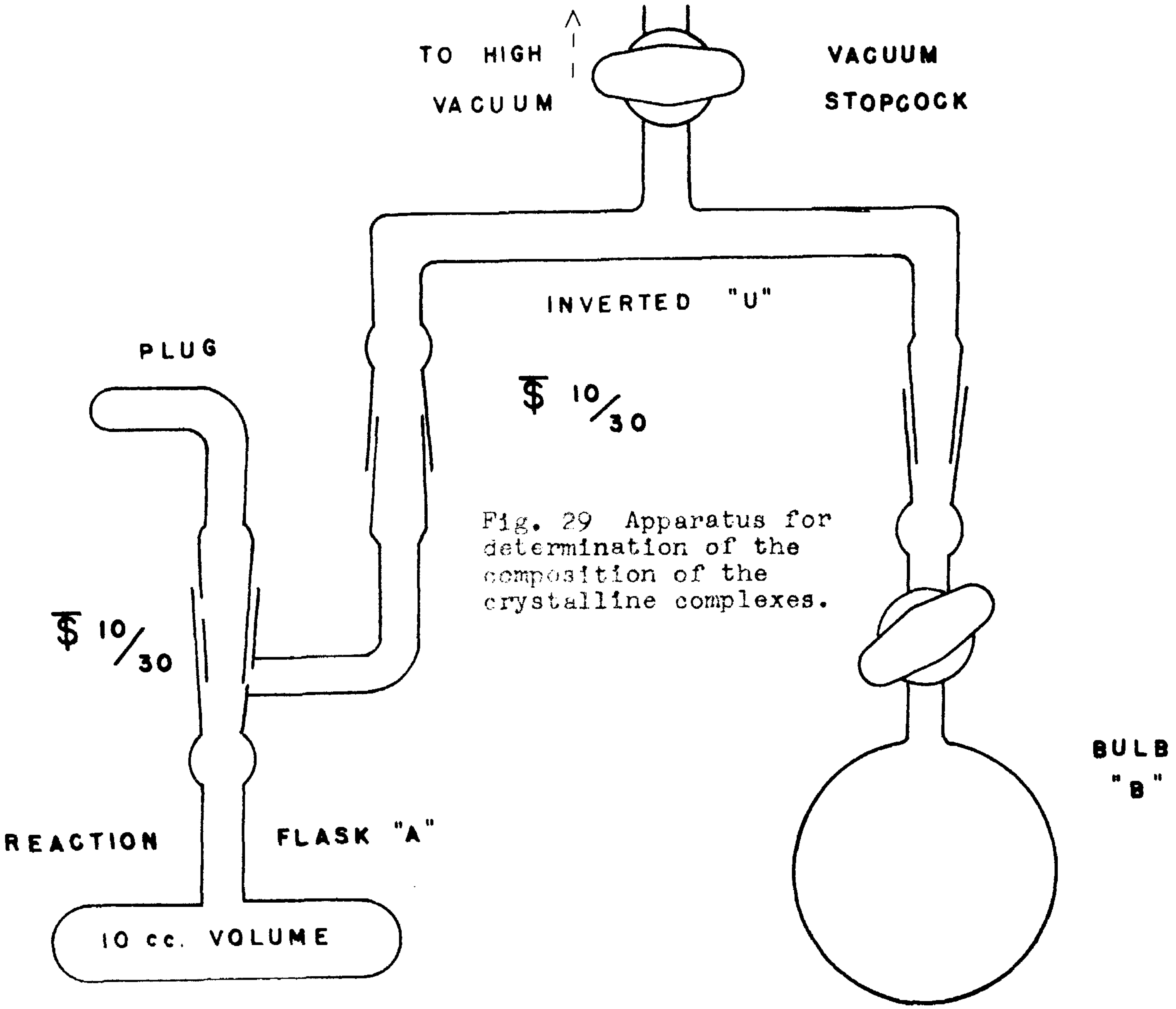

Fig. 29 Apparatus for determination of the composition of the crystalline complexes.

or a yellow (cuprous bromide) and a more opaque appearance.

A semi-wet sample of molecular complex where no liquid drops are apparent but part of the crystalline mass is semi-transparent can contain considerable excess organic component. This condition was observed in one trial determination of cuprous bromide-2-pentyne complex dried two hours with the reaction vessel "A" at 11° and the bulb "B" at 0°: the molar ratio of 2-pentyne to cuprous chloride was 3.18. If the temperature of the reaction vessel is too high local disturbances can cause a decomposed but wet sample of molecular complex (*e.g.*, cuprous bromide-2-pentyne, flask "A" at 20° and bulb "B" at 17°).

Experimental Results. Table 11 gives a list of the results and the conditions of the successful analyses. (Successful is defined as having obtained a dried but undecomposed sample of crystalline complex). In the case of 2-butyne and 2-pentyne complexes the total weight of the alkyne was corrected for the calculated weight of the gas phase above the crystals. For the purpose of Table 11 cuprous chloride is considered to be a monomer. In every case an analysis was terminated if the reaction vessel had leaked during shaking or drying.

This type of analysis is somewhat limited. The decomposition temperature must be near or above room temperature in order that a complete microscopic examination can be achieved before decomposition spontaneously takes place.

Table 11

Preparation and Analysis of Cuprous Halide-Ligand Complexes.

Complex	Ligand m.mole	CuX m.mole	n'	Temperature of reaction flask °C	Temperature of bulb "B" °C	Drying time hrs.	Ligand initial $n^{25}D$	Ligand recovered from cmplx. %	Ligand recovered from cmplx. $n^{25}D$	CuX from cmplx. color[a]
CuCl-2-Butyne	16.65	16.59	1.0036	25	0	12	1.3890	99.8	1.3891	S.Y.
CuCl-2-Butyne	18.38	18.36	1.0011	25	0	8	1.3890		1.3890	W.
CuCl-2-Pentyne	25.90	25.83	1.0027	10	-10	12		99.5		W.
CuCl-2-Pentyne	18.75	18.80	0.9973	10	-10	12	1.4006	99.9	1.4005	W.
CuCl-3-Hexyne	18.74	18.63	1.0060	25	0	12	1.4090	99.6	1.4087	W.
CuCl-3-Hexyne	18.63	18.65	0.9989	25	0	12	1.4090	99.5	1.4084	W.
CuBr-2-Butyne	14.22	14.21	1.0014	15	0	9	1.3890	99.1[b]	1.3890	S.Y.
CuBr-2-Butyne	16.62	16.58	1.0024	15	0	12				Y.
CuBr-2-Pentyne[c]	21.75	21.70	1.0023	8	0	5	1.4006	99.7	1.4007	S.Y.
CuBr-2-Pentyne[c]	18.31	18.26	1.0033	8	0	12				Y.
CuBr-3-Hexyne	21.33	21.42	0.9958	15	0	7	1.4089	99.3[d]	1.4087	Y.
CuBr-3-Hexyne	19.34	19.31	1.0016	15	0	9				Y.
CuCl-Aceto-nitrile	10.72	10.66	1.0060	5	0	3	1.3415	99.8	1.3414	W.
CuCl-Aceto-nitrile	12.32	12.28	1.0028	4.5	0	6	1.3410[e]	99.9	1.3408[e]	W.
CuBr-Aceto-nitrile	11.08	11.08	0.9997	ambient	0	4	1.3415	99.6	1.3415	Y.
CuBr-Aceto-nitrile	12.38	12.36	1.0015	ambient	0	6				Y.

[a] In this column W. means white, S.Y. means slightly yellow, Y. means yellow.

[b] Alkyne recovered in four hours using a hot water bath.

[c] According to the extrapolated P_c data these analyses were carried out under unstable conditions.

[d] Alkyne recovered in three hours using a hot water bath.

[e] Index of refraction at 26.4°.

From the method of analysis it might be expected that the organic component would be in slight excess over that calculated for a 1-to-1 complex. For example some alkyne might be dissolved in the stopcock grease. In six trials the average weight of the grease used in the stopcock was 20.5 mg.. Approximately 50 percent of the grease can come into contact with the organic phase without the apparatus leaking during the hours of shaking. It is conceivable to the author that 3 mg. of the organic phase could have been dissolved and retained by 10 mg. of grease under the conditions of the experiment. This would account for about 40 percent of the average excess of organic phase. Another probable source of error that would give a slight excess of organic phase over that expected would be the existence of the liquid phase in either the interstices of the crystalline mass and/or occluded in the individual crystals. It is indeed conceivable that, because of the narrow confines in the interstices giving rise to capillary effects, the saturated solution would be in equilibrium with the gaseous phase even when the crystals appeared dry.

In the cases where $n' < 1$ (n' is the ratio of the moles of ligand in the non-gaseous state to the moles of cuprous halide) it is suspected that the complete reaction of the cuprous halide to form the complex did not occur. Although large particles of cuprous halide would not go undetected, in the presence of the crystalline complex, very small particles of cuprous halide might be obscured.

H. DISSOCIATION VAPOR PRESSURE OF CRYSTALLINE COMPLEXES.

Introduction. The dissociation vapor pressure of six crystalline complexes has been determined at several temperatures between 7° and 37°. The equilibrium pressures have been approached by decomposition of the crystalline complexes (eq. 3), as well as by synthesis.

$$T = 25^{\circ} \qquad CuX{\cdot}Un_{sld.} = CuX_{sld.} + Un_{gas} \qquad \Delta h^{o}_{Dis.} \qquad (3)$$

In eq. 3 CuX is to be understood as either cuprous bromide or cuprous chloride, Un as an alkyne (either 2-butyne, 2-pentyne or 3-hexyne), and subscript sld. as referring to the solid state. For the purposes of this discussion the crystalline complexes shall be assumed to be monomers as indicated in eq. 3.

Theoretical. The dissociation constant $K_{Dis.}$ (eq. 4) can be expressed very simply if it is assumed that the activities, A, of solid complex and cuprous halide are unity, and that the fugacity of the alkyne φ_{Un}, is equal to the dissociation vapor pressure, P_c of the complex. The

$$K_{Dis.} = \frac{A_{CuX} \cdot \varphi_{Un}}{A_{CuX{\cdot}Un}} = P_c \qquad (4)$$

standard chemical potential change, $\Delta\mu^{o}_{Dis.}$, for the dissociation at 25° under equilibrium conditions is then expressed by eq. 5.

$$T = 25^{\circ} \quad \Delta\mu^{o}_{Dis.} = - RT \ln K_{Dis.} = - RT \ln P_c \qquad (5)$$

The heat of dissociation may be simply related to P_c as a function of absolute temperature as follows: Differentiate with respect to temperature at constant total pressure eq. 5 divided by the absolute temperature. This gives eq. 6 which may be rearranged to form eq. 7.

$$\left(\frac{\partial}{\partial T}\left(\frac{\Delta \mu^{o}_{Dis.}}{T}\right)\right)_P = -\frac{\Delta h^{o}_{Dis.}}{T^2} = -R\left(\frac{\partial \ln P_c}{\partial T}\right)_P \tag{6}$$

$$\left(\frac{\partial \ln P_c}{\partial T}\right)_P = \frac{\Delta h^{o}_{Dis.}}{R T^2} \tag{7}$$

Eq. 7 may be integrated, neglecting heat capacity effects, to form eq. 8, which manifests the relationship of $\Delta h_{Dis.}$ to P_c as a function of temperature. The simplified treatment above and other considerations elsewhere neglect the effects of pressure changes upon the chemical potential of the solids in spite of the fact that the author only assumes these effects are small. This assumption is probably justified since the pressure and hence, pressure differences, are small. Normally, of course, the standard chemical potential of a compound refers to its chemical potential at 25° and one atmosphere total pressure.

$$(\ln P_c)_{equil.} = -\frac{\Delta h^{o}_{Dis.}}{RT} + C' \tag{8}$$

<u>Experimental</u> <u>Results</u>. In each instance the cuprous halide was dissolved in excess alkyne to form a saturated

solution. The alkyne was then removed in small portions until the reaction flask contained a dry appearing crystalline mass. Vapor pressure measurements were then made until a constant dissociation vapor pressure was reached. From time to time additional alkyne was removed. Most dissociation vapor pressures were approached simply by raising or lowering the bath temperature and then determining vapor pressure until no further changes were noted. In some cases however, a subterfuge was used. For example, if a suspected equilibrium vapor pressure, P_c' at a known temperature had been previously approached from a lower pressure, the temperature of the reaction flask was then adjusted by raising or lowering the temperature of the flask until the vapor pressure was slightly greater than P_c' (by 2 to 20 mm. dependent upon the system). If the vapor pressure P_c' was then approached monotonically from this higher pressure it was considered that an equilibrium point had been determined.

Results. The dissociation vapor pressure data have been fitted by the method of least squares to a curve of the form of eq. 9. The values A and C with the mean devi-

$$\log P_c = A/T + C \tag{9}$$

ation of the data from the least squares curves are summarized for the systems studied in Table 12. A comparison of the experimental values with the calculated values

Table 12

Empirical Constants for the Determination of $P_{c_{cal.}}$

System	A	σ (A)	C	σ(C)	Mean Dev. mm.
CuCl 2-Butyne	-1989.53	0.40	8.9817	0.14	0.87
CuBr 2-Butyne	-2499.18	0.31	10.8629	0.11	0.87
CuCl 2-Pentyne	-3007.39	1.3	11.9218	0.014	0.54
CuBr 2-Pentyne	-1823.34	1.9	8.3981	0.021	2.10
CuCl 3-Hexyne	-3614.94	0.35	13.3454	0.039	0.08
CuBr 3-Hexyne	-3463.31	1.28	13.2324	0.11	0.39

σ is the standard deviation of the constants A and C.

In the following six tables the symbols in the Approach column denotes the following experimental conditions:

A, $P_{c_{ex.}}$ was approached from a higher pressure;

B, $P_{c_{ex.}}$ was approached from a lower pressure.

Table 13

Dissociation Vapor Pressure for the Cuprous Chloride-2-Butyne Complex.

Ex.	T °C	$P_{c_{ex.}}$ mm.	$P_{c_{cal.}}$ mm.	n'	Approach
1	25.02	200.9	204.1	0.943	B
2	24.98	204.2	203.7	0.943	A
5	8.43	82.7	82.6	0.927	B
6	8.43	82.6	82.6	0.927	A
8	14.86	118.3	118.7	0.919	B
9	14.87	118.4	118.8	0.919	A
10	18.14	142.0	142.0	0.915	B
11	21.75	173.8	172.2	0.907	B
12	21.76	173.9	172.2	0.907	A

Table 14

Dissociation Vapor Pressure for the Cuprous Bromide-2-Butyne Complex.

Ex.	T °C	$P_{c_{ex.}}$ mm.	$P_{c_{cal.}}$ mm.	n'	Approach
1	25.02	300.4	303.5	0.722	B
2	24.98	302.4	302.6	0.722	A
5	8.43	97.5	97.3	0.802	B
6	8.43	97.4	97.3	0.802	A
8	14.86	153.2	153.6	0.782	B
9	14.87	153.3	153.7	0.782	A
10	18.14	192.2	192.4	0.767	B
11	21.75	247.0	245.0	0.745	B
12	21.76	246.9	245.1	0.745	A

Table 15

Dissociation Vapor Pressure for the Cuprous Chloride-2-Pentyne Complex.

1	25.02	67.2	68.7	0.735	B
2	24.98	68.2	68.4	0.623	A
8	14.86	30.1	30.3	0.630	B
9	14.87	30.2	30.3	0.630	A
10	18.14	39.7	39.7	0.628	B
11	21.75	53.9	53.1	0.625	B
12	21.76	54.1	53.1	0.625	A
6*	8.43	20.3	17.5	0.632	A
7*	8.43	18.4	17.5	0.632	B

* Data not included in least squares treatment.

Table 16

Dissociation Vapor Pressure for the Cuprous Bromide-2-Pentyne Complex.

1	25.02	189.4	192.1	0.849	B
2	24.98	189.8	192.7	0.849	A
8	14.86	115.4	116.9	0.869	B
9	14.87	115.7	117.0	0.869	A
10	18.14	142.2	137.8	0.862	B
10'	18.14	142.2	137.8	0.611	B
11	21.75	165.8	164.4	0.604	B

Table 16 (continuation)

Ex.	T °C	$P_{c_{ex.}}$ mm.	$P_{c_{cal.}}$ mm.	n'	Approach
12	21.76	165.9	164.4	0.604	A
5*	8.43	67.8	83.8	0.880	B
6*	8.43	67.8	83.8	0.880	A

* Data not included in least squares treatment.

Table 17

Dissociation Vapor Pressure for the Cuprous Chloride-3-Hexyne Complex.

72	7.33	2.8	2.9	0.831	B
73	13.34	5.3	5.4	0.830	B
74	15.24	6.5	6.5	0.830	B
75	17.73	8.3	8.3	0.829	B
76	19.91	10.3	10.3	0.829	B
79	29.70	25.7	25.7	0.823	B
80	22.18	12.8	12.8	0.828	A
81	24.74	16.2	16.3	0.826	B
82	32.37	32.4	32.7	0.820	B
83	36.80	48.3	48.2	0.814	B
84	34.90	41.0	40.9	0.817	A
87	13.26	5.4	5.3	0.830	A
88	11.14	4.4	4.3	0.831	A

Table 18

Dissociation Vapor Pressure for the Cuprous Bromide-3-Hexyne Complex.

1	25.02	41.1	41.5	0.987	B
2	24.98	41.9	41.4	0.828	A
3	24.96	40.3	41.3	0.828	A
4	8.41	8.6	8.6	0.834	A
5	8.43	8.6	8.6	0.834	B
6	8.43	8.7	8.6	0.834	A
8	14.86	15.9	16.2	0.833	B
9	14.87	16.0	16.2	0.833	A
10	18.14	21.9	21.9	0.832	B
11	21.75	32.3	30.9	0.824	B

LOG P_c vs. $^1/_T$

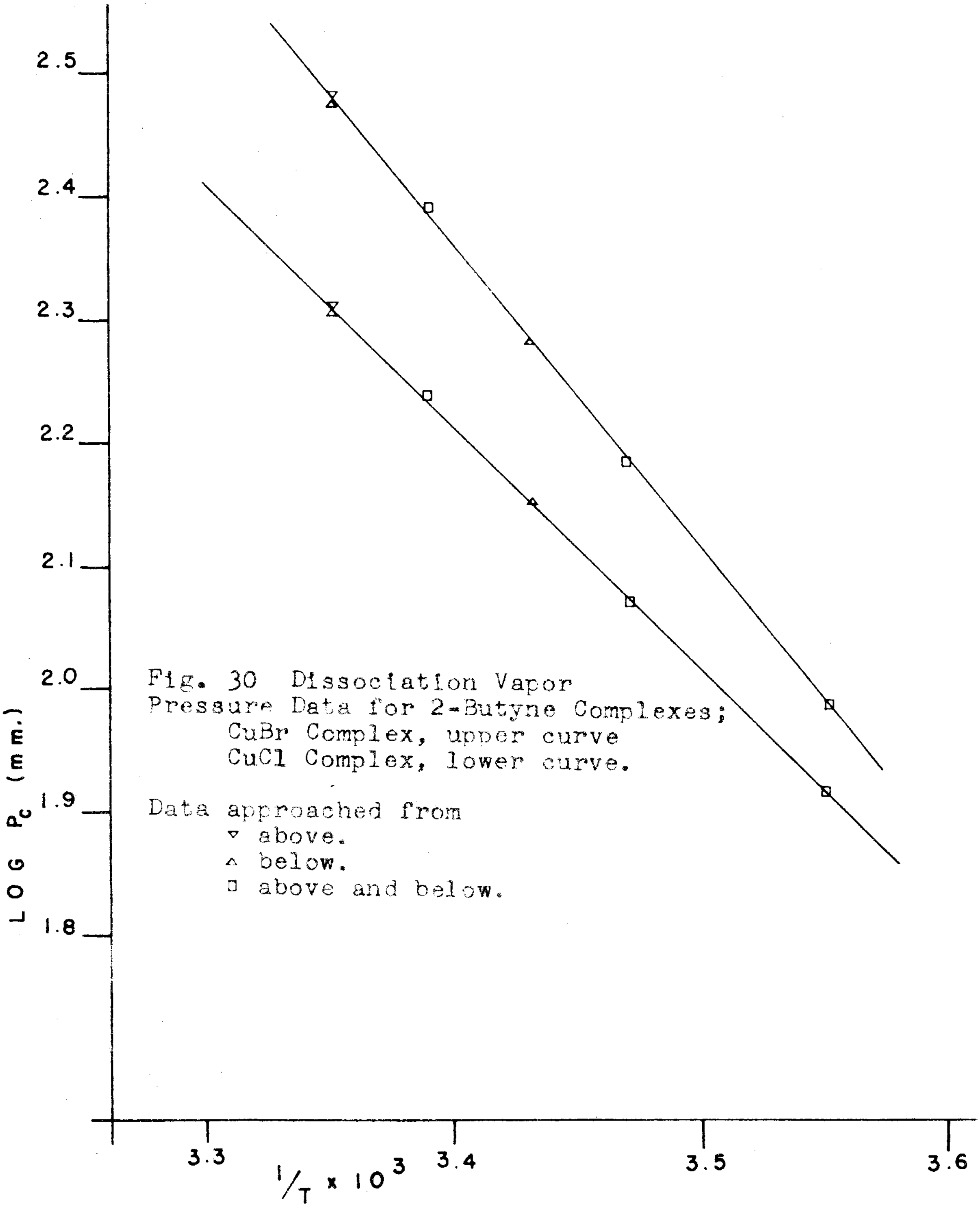

Fig. 30 Dissociation Vapor Pressure Data for 2-Butyne Complexes;
CuBr Complex, upper curve
CuCl Complex, lower curve.

Data approached from
▽ above.
△ below.
□ above and below.

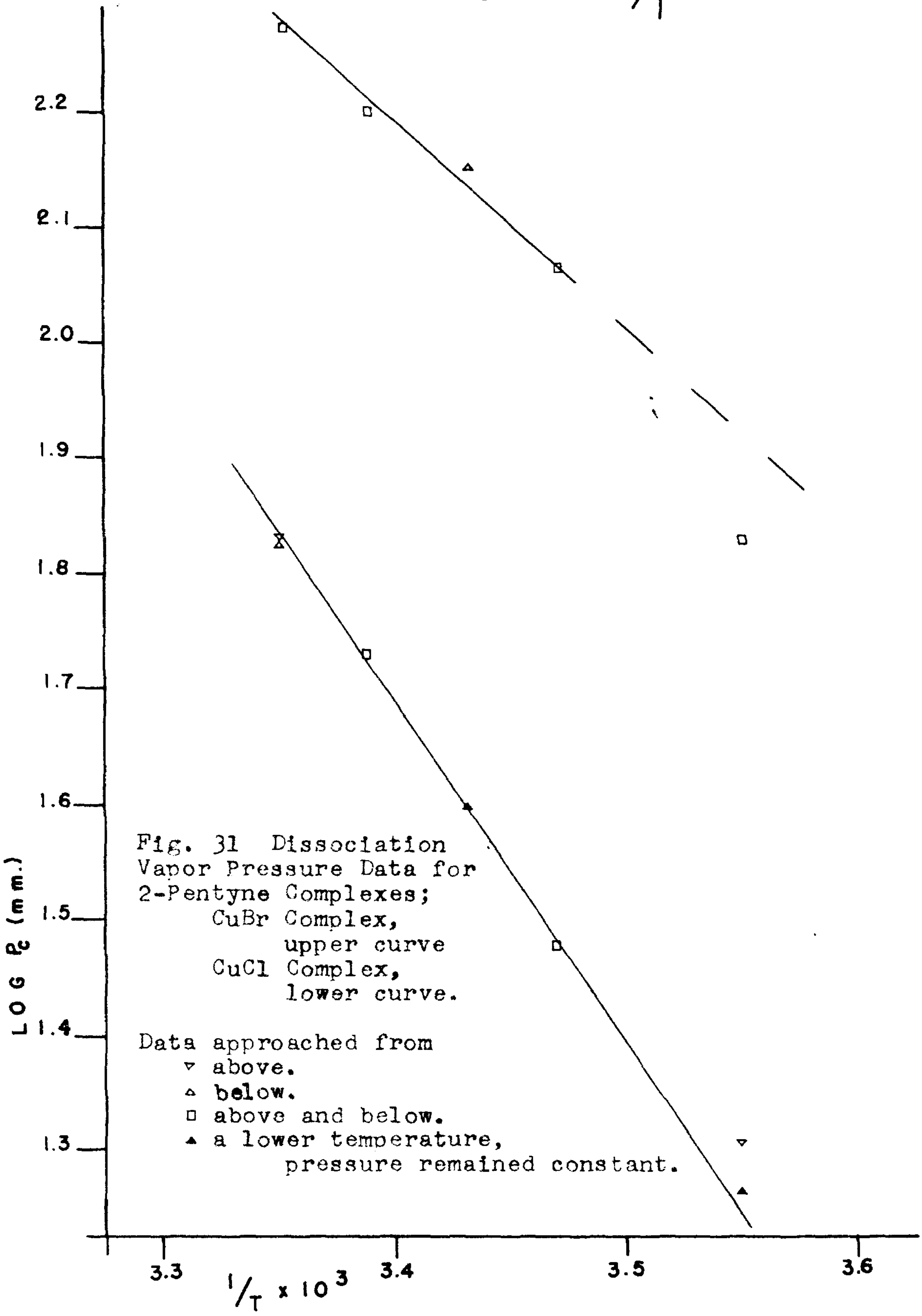
LOG P_c vs. $1/T$

Fig. 31 Dissociation Vapor Pressure Data for 2-Pentyne Complexes;
CuBr Complex, upper curve
CuCl Complex, lower curve.

Data approached from
- ▽ above.
- △ below.
- □ above and below.
- ▲ a lower temperature, pressure remained constant.

LOG P_c vs. $1/T$

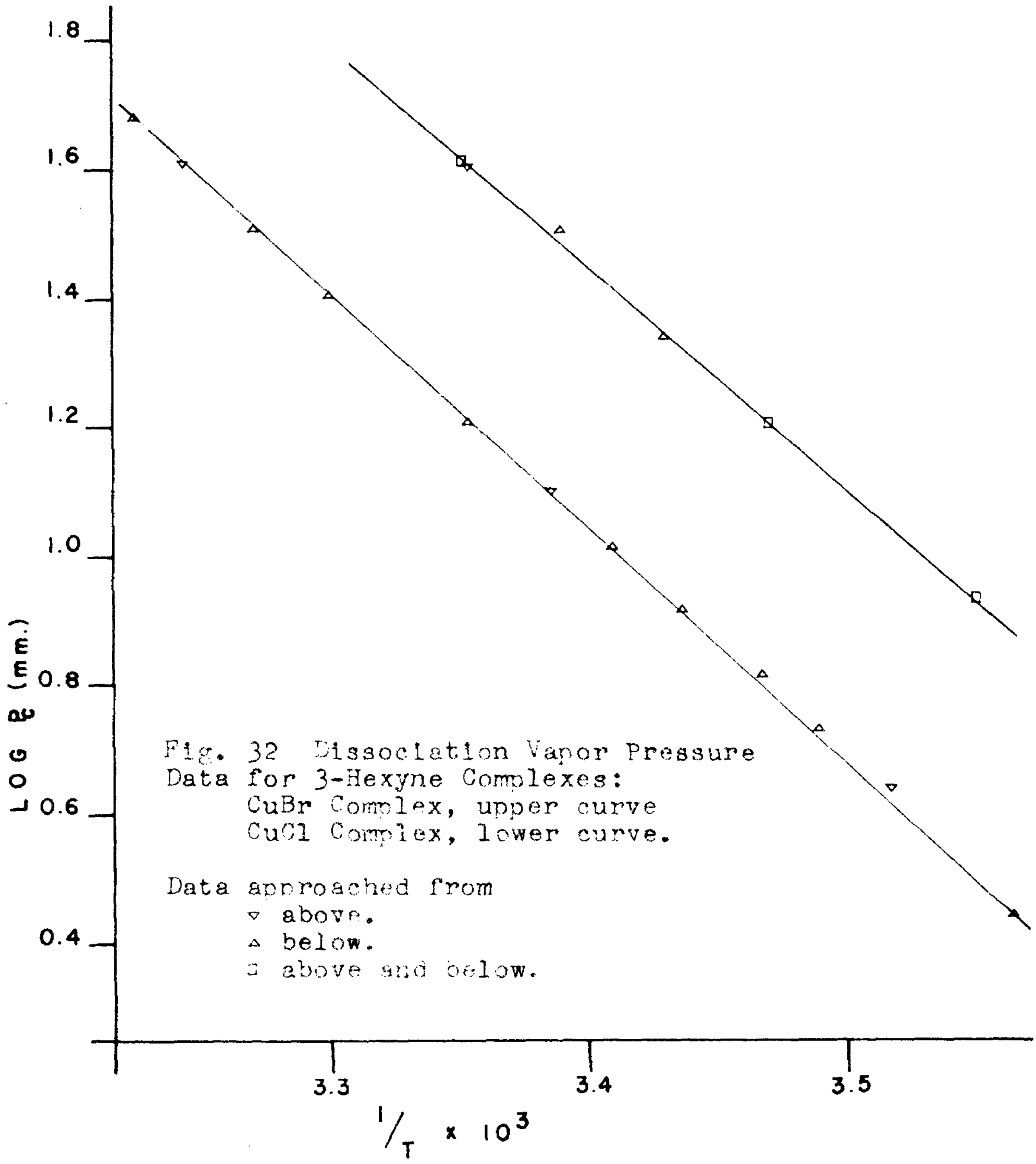

Fig. 32 Dissociation Vapor Pressure Data for 3-Hexyne Complexes:
CuBr Complex, upper curve
CuCl Complex, lower curve.

Data approached from
▽ above.
△ below.
□ above and below.

for each system is given in Tables 13 to 18. The data from Ex. 6 and 7 for the system cuprous chloride 2-pentyne (Table 15) and Ex. 5 and 6 (Table 16) for the system cuprous bromide 2-pentyne were not included for the least square treatment. The ratio, n', of the moles of alkyne in the solid phase to that of the cuprous chloride is also given in the above mentioned tables. The agreement of the $P_{c_{ex.}}$ with $P_{c_{cal.}}$ for the equilibrium values is seen to be satisfactory for all the systems except cuprous bromide 2-pentyne (see Fig. 30, 31, and 32).

Deviations of the measured dissociation vapor pressures of the cuprous bromide-2-pentyne complex from the calculated values, $P_{c_{cal.}}$, were greater than the estimated maximum error 0.4 mm.. Indeed, Ex. 10 and 10' for this system (Table 16) have the largest deviation (4.4 mm.) of $P_{c_{ex.}}$ from $P_{c_{cal.}}$ observed in any system studied. Furthermore even though P_c was approached from below, still $P_{c_{ex.}} > P_{c_{cal.}}$. It was also demonstrated that the cuprous bromide was not protected by a coat of crystalline complex which would prevent the absorption of the alkyne and, hence, explain this deviation. An amount of the alkyne far in excess over that necessary to account for the deviation was removed at constant temperature (18.14°). The pressure was then recorded as a function of time. It approached the value listed in Ex. 10' (Table 16). In addition to the above discrepancy at 18.14° there is a much larger discrepancy between $P_{c_{ex.}}$ and $P_{c_{cal.}}$ for the cuprous bromide 2-pentyne system at 8.43°. Inasmuch as this pressure $P_{c_{ex.}}$ has been approached from higher and lower pressures it would be virtually impossible to discount the discrepancy (16 mm.) as an experimental error. Furthermore it will be noticed from Table 11 that the analysis of the cuprous bromide-2-pentyne complex was accomplished successfully at 8° under conditions for which the P_c(79 mm.) (extrapolated from higher temperature measurements) was greater than P_o(72 mm.) the vapor pressure of the pure alkyne at 0°. However, between 14.9° and 8.43° it is possible that a phase transition has taken place. Hence, $P_{c_{ex.}}$ at 8.43° could be interpreted as a typical point on another curve of the form eq.8, with different values of $\Delta h^{o}_{Dis.}$ and C' in the region of 8.4° from those at, say, 25°. In general when a ligand forms several complexes of different composition with the cuprous halides, the composition of the stable complexes tends toward that of the cuprous halide as the temperature is increased (38). In view of this fact it may be deduced from a knowledge of the pressure discrepancy (16 mm.), the volume of the system at 8.43° (78.4 ml.), the composition of the complex at 8° and the ratio n' (Table 16), that the composition of the crystalline material stable at 25° is the same as that at 8° ($CuBr{\cdot}C_5H_8$). However, until the hypothesis, that there is a transition point between 14.9° and 8.43° in the cuprous bromide 2-pentyne system, is verified by more extensive experimental evidence, the possibility of the second order transition cannot be excluded.

The heats of vaporization of pure alkynes, given previously in this thesis, are summarized in Table 19 with the various heats of dissociation $\Delta h^{o}_{Dis.}$ as determined from the A/T term of eq. 9. Table 19 includes the calculated dissociation pressures P_c at 25°, and the standard chemical potential difference, $\Delta \mu^{o}_{Dis.}$, for the dissociation reaction (eq. 3) at equilibrium.

Table 19

Thermodynamic Data for the Dissociation of the Complexes into Gaseous Alkyne and Solid Cuprous Halide.

Alkyne	Pure	Cuprous Chloride			Cuprous Bromide		
	$\Delta h_{vap.}$	$\Delta h^{o}_{Dis.}$	$P_{c_{cal.}}$	$\Delta \mu^{o}_{Dis.}$	$\Delta h^{o}_{Dis.}$	$P_{c_{cal.}}$	$\Delta \mu^{o}_{Dis.}$
2-Butyne	6.67	9.10	203.9	-3.16	11.40	303.0	-3.39
2-Pentyne	7.61	13.76	68.6	-2.50	8.34	191.9	-3.12
3-Hexyne	8.54	16.53	16.7	-1.67	15.84	41.5	-2.20

T = 25°. $\Delta h^{o}_{Dis.}$, $\Delta \mu^{o}_{Dis.}$ in Kcal/mole , $P_{c_{cal.}}$ in mm..

Discussion of Results. For each alkyne the cuprous chloride complex is seen to be more stable than the cuprous bromide complex at 25°. The heats of dissociation of the complexes, however, are seen to vary widely, but in only one case (2-butyne) is the heat of dissociation for the cuprous bromide complex greater than for the chloride.

An interesting reaction to discuss is that of the solid cuprous halide with the pure liquid alkyne to form the solid complex (eq.10) at 25°. The heats of dissociation Δh_L and the chemical potential changes $\Delta \mu_L$ can be calculated

$$T = 25^\circ. \qquad CuX \cdot Un_{sld.} = CuX_{sld.} + Un_l(\text{pure}) \qquad \Delta h_L \quad (10)$$

from eq. 11 and 12. The values of Δh_L, $\Delta \mu_L$, and Δs_L

$$\Delta h_L = \Delta h^o_{Dis.} - \Delta h_{vap.} \qquad (11)$$

$$\Delta \mu_L = RT \ln \frac{P_o}{P_c} \qquad (12)$$

are given in Table 20 for each system. The changes of entropy for the reaction described above show remarkable variations. If the crystalline complexes were of a comparable nature in their energy distributions it might be expected

Table 20

Thermodynamic Data for the Dissociation of the Complexes into the Pure Liquid Alkyne and Solid Cuprous Halide.

Alkyne	Cuprous Chloride			Cuprous Bromide		
	Δh_L	$\Delta \mu_L$	Δs_L	Δh_L	$\Delta \mu_L$	Δs_L
2-Butyne	2.43	0.54	6.4	4.73	0.37	14.6
2-Pentyne	6.15	0.54	18.8	0.73	0.09	2.1
3-Hexyne	7.99	0.71	24.4	7.30	0.31	23.4

$T = 25^\circ$. Δh_L, $\Delta \mu_L$ in Kcal/mole , Δs_L in cal/mole.°

that Δs_L would demonstrate a gradual increase in the order 2-butyne < 2-pentyne < 3-hexyne. The complexes cuprous chloride-2-butyne and cuprous bromide-2-pentyne, however, showed marked deviations from this expected increase in Δs_L. Is there then, something special about these two crystalline complexes in comparison to the others?

As indicated above (page 98) in the discussion of the system cuprous bromide 2-pentyne the question can in part be answered with a tentative yes. More explicitly, it can be suggested that there is another phase existent below 8.43° for the cuprous bromide 2-pentyne system; and that this phase has a Δh_L for the reaction above (eq. 10), which is comparable with the Δh_L for the system cuprous chloride 2-pentyne. The as yet unstated premise from which this suggestion has been developed will be the subject of a later discussion.

Decomposition Temperature. A crystalline complex will dissociate when the vapor pressure of the ligand falls below P_c, the dissociation vapor pressure. This condition may occur when the ligand is in equilibrium with another phase. Three possible other phases are: another crystalline complex, the pure liquid ligand and a ligand solution of crystalline complexes.

The decomposition temperature of a complex may be defined (12) as that temperature at which the dissociation vapor pressure of the complex is equal to the vapor pressure of the pure ligand (presumed to be organic) following eq.13.

$$\Delta\mu = 0 \qquad CuX{\cdot}Un_{sld.} = CuX_{sld.} + Un_1(\text{pure}) \tag{13}$$

Hence, in the present case at the decomposition temperature T_d, $P_c = P_o$. Some sanction for this special designation can be derived from the following thermodynamic considerations:

(i) for the reaction of eq. 13 Δh and $\Delta\mu$ has the relationship of eq. 14 and 15,

$$\Delta h = \Delta h_L = \Delta h_{Dis.} - \Delta h_{vap.} \tag{14}$$

$$\Delta\mu = \Delta\mu_L = 0 \tag{15}$$

(ii) there are zero degrees of freedom at this temperature since there are four phases ($CuX{\cdot}Un_{sld.}$, $CuX_{sld.}$, Un_1, and Un_{gas}) and two components, and

(iii) for $T > T_d$ there can be no vapor phase in equilibrium with the crystalline complex.

Table 21 includes the calculated decomposition temperature $T_{d_{cal.}}$ and the corresponding pressure $P_{d_{cal.}}$ ($P_{d_{cal.}} = P_{c_{cal.}} = P_{o_{cal.}}$ at $T_{d_{cal.}}$) for the six systems studied. These were calculated from the simultaneous solution of the appropriate equations of the form eq. 9 and 2 respectively. Although these equations neglect possible heat capacity effects for the corresponding reactions, it may be noted that the simultaneous solution of two such equations is equivalent to the assumption that the coefficients of the log T term are equal. In actual practice this equivalence is unlikely.

Table 21

Calculated Decomposition Temperature and Pressure for the Cuprous Halide-Alkyne Complexes.

Alkyne	Cuprous Chloride		Cuprous Bromide	
	$T_{d_{cal.}}$ °C	$P_{d_{cal.}}$ mm.	$T_{d_{cal.}}$ °C	$P_{d_{cal.}}$ mm.
2-Butyne	155	22×10^3	60.3	23.3
2-Pentyne	65.6	1105	87.2	2179
3-Hexyne	66.0	487	43.5	198

However, the discrepancy in the answer $T_{d_{cal.}}$ due to this assumption may be small. The same argument, however, does not apply to $P_{d_{cal.}}$. The discrepancy ($P_{d_{cal.}} - P_{d_{ex.}}$) would be expected to increase as T_d increases.

In the present cases, however, the above mentioned $P_{d_{ex.}}$ is not expected to exist experimentally because (assuming there is no phase change of the crystalline complex) before $T_{d_{cal.}}$ is reached the complex may become unstable with respect to the saturated solution since the present complexes (or the cuprous halide) are known to be soluble in excess alkyne. If the vapor pressure of the saturated solution is designated as P_s then the crystals will actually decompose under equilibrium conditions when $P_c = P_s$. Hence, as the temperature increases, at the actual decomposition temperature T_d' under equilibrium conditions, the dry crystalline complex may be expected to dissociate to the solid cuprous halide* and a saturated solution, the vapor pressure of which is P_s. Since T_d' may be expected to be lower than $T_{d_{cal.}}$ in this case, $T_{d_{cal.}}$ will be unrealizable experimentally and hence represent an artificial value.

Reversal of Relative Stability. At 25° for each alkyne (2-butyne, 2-pentyne and 3-hexyne) the cuprous chloride complex is more stable than the bromide analogue. At what temperature T_R is this no longer true? The question can be rephrased in the following manner; at what temperature T_R is the chemical potential change $\Delta\mu_R$, equal to zero for the reaction below (eq. 16)? Table 22 gives T_R, the

$$CuCl_{sld.} + CuBr\cdot Un_{sld.} = CuCl\cdot Un_{sld.} + CuBr_{sld.} \qquad (16)$$

corresponding vapor pressure P_R, the heat of reaction Δh_R, and the entropy change Δs_R for the 2-butyne and 2-pentyne systems. Heat capacity effects are neglected. Since for 3-hexyne T_R is seen to be much greater than T_D for either complex only the signs are indicated for Δh_R and Δs_R.

As can be seen from Fig. 30 the intersection of the two log P_c curves for 2-butyne will be below room temperature as indicated in the following table. The reaction

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* As there is no evidence to the contrary, it is assumed, here and elsewhere in this thesis, that a crystalline melt will not be formed where $n' < 1$.

Table 22

Thermodynamic Data for the Complex Substitution Reaction of Equation 16.

Alkyne	$T_{R_{cal.}}$ °C	$P_{R_{cal.}}$ mm.	Δh_R Kcal/mole	Δs_R cal/mole°
2-Butyne	-2.27	43.4	2.30	8.49
2-Pentyne	62.8	937	-5.42	-16.13
3-Hexyne	1068			

(eq. 16) is accompanied by an increase in entropy. The corresponding reaction for the cuprous halide 2-pentyne system, however, has an entropy change which is negative and large in magnitude. T_R for 2-pentyne is above room temperature as Fig. 31 and Table 22 indicate. However, since this T_R is very near to T_D for each of the two complexes (cuprous chloride-2-pentyne and cuprous bromide-2-pentyne) and since the solubility of the complexes are very high (see Table 26) it is not expected that T_R can be realized experimentally for the reasons stated above concerning the artificial nature of $T_{d_{cal.}}$.

Since the entropies of the crystalline cuprous chloride and cuprous bromide at 25° are 20.8 and 21.9 calories per mole°(39), it is seen that the entropy at -2.27° of cuprous chloride-2-butyne complex is appreciably greater than that of the bromide analogue. For the 2-pentyne system the reverse situation would be true at 62.8°.

In the known cuprous halide-alkene and-alkyne complexes the cuprous chloride complex is always more stable than the corresponding bromide (12), hence, it would not be surprising if a crystal structure transition took place in the cuprous chloride 2-butyne system above or near -2.27°.

Phases α and β. Thermodynamic data as obtained from the above dissociation vapor pressure measurements suggest the hypothesis that there exist at least two different kinds of crystalline cuprous halide complexes. Thermodynamically these phases, which will be denoted by α and β, are characterized by widely different entropies for the reaction of eq. 10.

$$T = 25^{\circ}. \quad CuX \cdot Un_{sld.} = CuX_{sld.} + Un_{l}(pure) \qquad (10)$$

Crystalline phase α is defined for each alkyne system as that phase which has a large entropy change for the above dissociation reaction. Crystallographically it might be expected that phase α has little disorder and that the thermal vibrations of the alkyne molecules are small. In phase β, characterized by a small entropy change for the above dissociation reaction, disorder or large thermal vibrations might be expected. Hence, phase β might be considered as a high temperature modification of the complex and the α phase as stable at a lower temperature. Structural similarities are expected to exist among the various members of each phase. Crystallographically, however, the members of a phase might be expected to belong to different space groups. Hence, the α phase may consist of only trimers or tetramers or chains of the complex CuX•Un packed in the crystal differently for each member, and the β crystals composed of packed monomers or dimers.

The known members of the α phase are considered to be cuprous bromide-2-butyne, cuprous chloride-2-pentyne, cuprous chloride-3-hexyne, and cuprous bromide-3-hexyne. Photomicrographs (Fig. 14, 17, and 24) indicate morphological similarities of the cuprous bromide-2-butyne, cuprous chloride-3-hexyne and cuprous bromide-3-hexyne complexes to one another. The latter two complexes are considered to be isomorphous. The low temperature modification of the cuprous bromide-2-pentyne complex (discussed on page 98) may be of the α phase. The unusual behavior of the cuprous chloride 2-butyne system in comparison with the bromide analogue (above) suggests that the so-called α phase may exist for cuprous chloride-2-butyne as well. The cuprous chloride-2-butyne and cuprous bromide-2-pentyne complexes at 25° are considered to be members of the β phase.

The above description of possible α and β phases may be summarized by saying that the cuprous halide-alkyne crystalline complexes may exist as either α or β phases depending upon the temperature.

It is recognized by the author that the above hypothesis is only suggested by the available evidence and that its final verification awaits further experimentation, preferrably of a thermodynamic and structural nature.

Rate of Attainment of Equilibrium. The rate at which the measured pressure, P, approached the equilibrium dissociation vapor pressure, P_c, depended not only upon the system but also upon the history of the system.

Under favorable conditions equilibrium was attained in six days for the systems cuprous chloride 2-butyne, cuprous bromide 2-butyne; in six hours for the systems cuprous chloride 2-pentyne, cuprous chloride 3-hexyne; and in three hours for the systems cuprous bromide 2-pentyne, cuprous bromide 3-hexyne. Typical examples of the rate of approach of P to P_c are indicated in Fig. 33 for some of the systems. The approaches by synthesis and by decomposition of the complex were approximately at the same rate. For the last four mentioned systems 24 hours of equilibration time were allowed before equilibrium was considered established.

It appears that "favorable conditions" do not in general include mechanical stirring. The cuprous halide in the systems where the dissociation vapor pressure was being determined was prepared by the dissociation of the crystalline complex. It is possible that cuprous halide freshly prepared in this manner had a special relationship (unstated) to the remaining crystalline complex which facilitates the synthesis of the complex when $P > P_c$. If this were the case then it would be expected that any thing

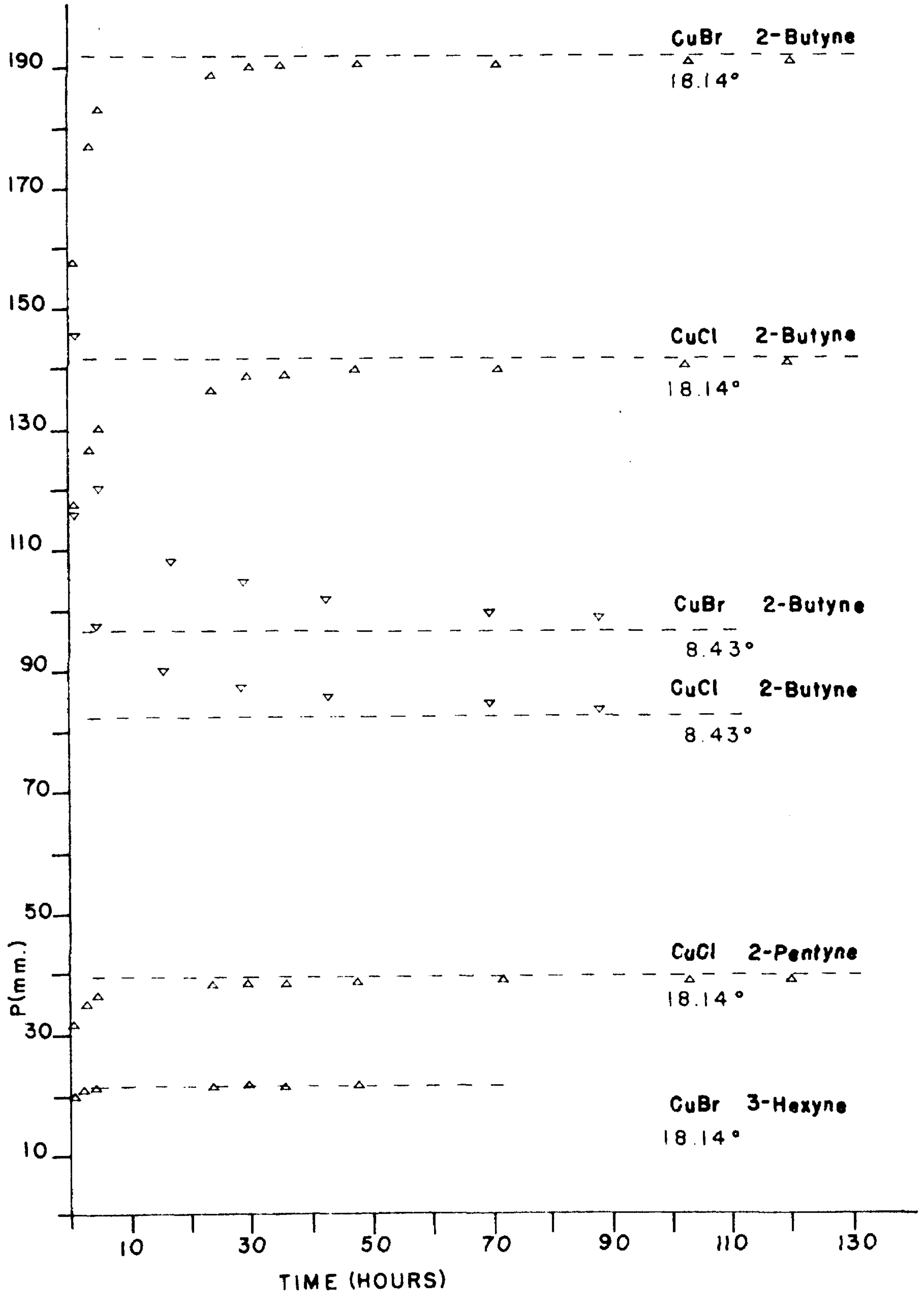


Fig. 33 The approach of P to P_c at different temperatures under favorable conditions for various systems. No mechanical stirring was employed.
▽ initial pressure > $P_{c_{cal.}}$, △ initial pressure > $P_{c_{cal.}}$

(like mechanical stirring) that disturbed the special relationship would decrease the absolute rate of equilibrium attainment.

That the rate of attainment of equilibrium was dependent upon the history of the system is indicated in the examples below.

Cuprous Chloride 2-Butyne. The data of Table 23 were recorded for the system cuprous chloride 2-butyne at 0°. The equilibrium dissociation vapor pressure based on experimental data at and above 8.4° at this temperature was 50 mm.. When P was plotted as a function of time a smooth curve was obtained for each case. It is remarkable to note that cases 1 and 2 represent synthesis very near to equal molar amounts of the alkyne and cuprous chloride with the attainment of the equilibrium vapor pressure.

Table 23

Non-Equilibrium Dissociation Vapor Pressure Data for the Cuprous Chloride-2-Butyne Complex at 0°.

Case	Obs. No.	Time of obs. hrs.	$P_{in.}$ mm.	P_{final} mm.	ΔP mm.	$n'_{equi.}$	Approach
1	4	71	53.3	50.1	0.9	0.992	A
2	6	84	53.3	50.1	0.8	0.992	A
3	8	88	29.0	42.5	0.2	0.992	B
4	13	134	5.3	32.7	6.5	0.901	B

Obs. = number of observations, $P_{in.}$ = initial pressure observation, ΔP = pressure change during last 40 hours of observation, $n'_{equi.}$ = calculated molar ratio of non-gaseous alkyne to cuprous chloride under equilibrium conditions. In the approach column, A means $P_{in.} > P_{final.}$, B means $P_{in.} < P_{final.}$

The change of pressure ΔP, during the last 40 hours of observation indicates the approach of P to P_c was asymptotic for these two cases. After the reaction flask had been carefully chilled to -78° and after one hour at this temperature, then had been allowed to warm to 0°, the pressure approached asymptotically 42.5 mm. (Case 3) instead of the expected 50.0 mm.. A conceivable explanation of this behavior resides in the postulated α phase for cuprous chloride 2-butyne.

In Case 4 2-butyne was slowly removed at constant temperature, 0°. Within the time of the experiment, 34 hours, however, ΔP indicated that decomposition was still occurring and that an equilibrium pressure had not yet been reached. This effect has not been observed in any other system studied. The 'nucleated' decomposition of cuprous chloride-2-butyne discussed previously (page 82) may offer an explanation for the anomalous behavior of both Cases 3 and 4. If the crystalline complex is not crystallographically imperfect (i.e. containing dislocations on the surface of a crystal in contact with the gaseous phase) then synthesis or decomposition may be expected to occur with comparative ease. However, if, in the case of decomposition very few imperfect crystals are present and the majority are crystallographically perfect, (conversely restricted as above) then it may be expected that decomposition will occur until either

P_c is reached or all the imperfect crystals are decomposed (32). If the latter is the case and P is still less than P_c a plateau in the time plot of P, or a pseudo-equilibrium dissociation pressure, might be observed until the decomposition process is reinitiated.

Cuprous Chloride 2-Pentyne. At 8.43° the decrease of P to a constant value 20.3 mm. (see page 93, Table 15, Ex. 6; and page 96, Fig. 31) was observed; the time of observation was 10 days. The temperature was then decreased until P measured 12.2 mm.. Upon increasing the temperature to 8.43° P remained constant for 60 hours. This indicated that the value 20.3 mm. as obtained by synthesis did not represent an equilibrium pressure. The temperature was again lowered until P was 18.4 mm.; after increasing the bath temperature to 8.43° this reading did not change significantly during the observation time of 9 days (Table 15 Ex. 7). The relations of $P_{ex.}$ of Ex. 6 and 7 to $P_{c_{cal.}}$ are indicated graphically in Fig. 31 at $1/T \times 10^3 = 3.551$.

Cuprous Chloride 3-Hexyne. In this system,like the one above,the experimental vapor pressure indicated that an equilibrium condition was not obtained even though excess cuprous chloride was present in both systems. Two possible reasons for this are evident:

(i) the cuprous chloride exposed to the gaseous alkyne was inactive possibly because of mechanical stirring,

(ii) the excess cuprous chloride was covered or coated by the crystalline complex so that direct contact with the gaseous phase was not achieved.

Table 24 compares a set of non-equilibrium dissociation vapor pressure determinations P_c' with $P_{c_{cal.}}$ as a function of increasing temperature. The history of this system was as follows: a saturated solution of cuprous chloride and 3-hexyne at 38.36°, $P_s = 57.6$ mm., was cooled to 23.95° ($n = 0.954$). Crystalline complex appeared as a solid dry mass, and the vapor pressure had dropped to P'. At constant temperature 3-hexyne was removed until $n = 0.881$ and $P = 0.2$ mm. $<$ P'. The vapor pressure then increased to a constant 14.9 mm. (Ex. 61). The temperature of the system was then increased and the vapor pressure determined as a function of time. The final values, $P'_{ex.}$, the temperature, and the hours of observation are given in Table 24. That

Table 24

Non-Equilibrium Dissociation Vapor Pressure Data for the Cuprous Chloride-3-Hexyne Complex.

Ex.	Observation time hrs.	T °C	$P'_{c_{ex.}}$ mm.	$P_{c_{cal.}}$ mm.	Approach
61	24	23.95	14.9	15.1	B
62	12	26.98	20.2	20.0	B
63	10	27.47	21.7	21.0	B
64	17	32.24	31.8	32.3	B
65	48	36.91	47.7	48.7	B

Mechanical stirring in these experiments was continuous. $n = 0.881$. In the Approach column, B indicates that the experimental but non-equilibrium vapor pressure, $P'_{c_{ex.}}$ was approached from a lower pressure at a lower temperature.

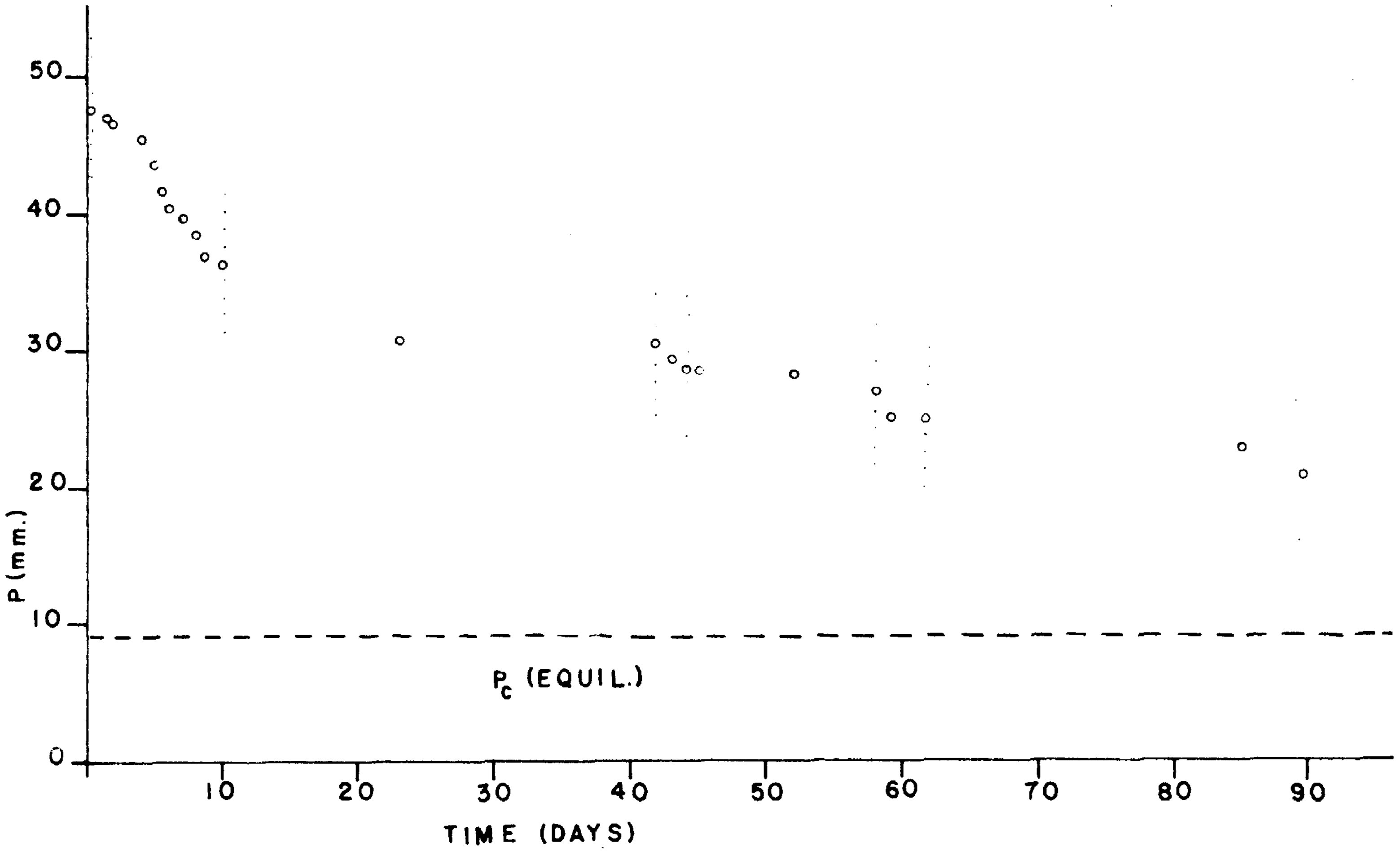


Fig. 34 The approach of P to P_c for the cuprous chloride 3-hexyne system at 13.6° under unfavorable conditions. Between the vertical dotted lines mechanical stirring was continuous.

these values P_c' are not equilibrium values even though the time of observation was larger than that required under favorable conditions (6 hours) is indicated by the fact that no significant synthesis took place when the bath was lowered to 18.6°. Fig. 34 shows that the equilibrium value ($P_c = 9.1$ mm.) was not reached even after 89 days of observation. The effect of mechanical stirring (which did not break up the large masses of complex) accelerated the synthesis of the complex. However, compared to the 6 hours required to synthesize the complex without stirring under favorable conditions, this acceleration was negligible. It is noteworthy that in this case not only was cuprous chloride in considerable excess, but also that some cuprous chloride had just been formed by decomposition. However, since stirring had been continuous during the experiments listed in Table 24 the relationship of the freshly prepared (by dissociation) cuprous chloride to the remaining associated crystalline complex was unknown. The evidence above led the author to believe that mechanical stirring may be a deterrent to the synthesis of the complex from the solid cuprous halide and a gaseous alkyne under certain conditions. Accordingly mechanical stirring was not employed in obtaining the data listed in Tables 13 to 18.

Experimental Details. The cuprous chloride 3-hexyne system was studied in reaction flask type No. 2. The other systems employed reaction flask type No. 1.

Cuprous chloride and cuprous bromide as freshly prepared on pages 29 and 32 respectively were introduced into the respective flask in the following manner: the reaction flasks which had been degassed as described on page 23 were filled with nitrogen at a somewhat greater (ca. 5 mm.) than atmospheric pressure. For the reaction flask type No. 1, the vacuum side of the manometer was simultaneously filled with nitrogen so that there was no movement of the mercury columns. A short section of the stem S (see Fig. 9 and 10) of the appropriate reaction flask was then removed and the cuprous halide introduced into the flasks through a tared funnel. The stem was then sealed by removing a section of it in such a manner that no water from the flame was introduced into the reaction flask. During this entire procedure a gentle stream of nitrogen was flushing through the flask and out the stem. The amount of cuprous halide introduced into each system is listed below in Table 25. After the flask had been evacuated and degassed for 10 days the alkynes (prepared as described on pages 62 and 63) were introduced from storage. The volumes of the reaction flasks at zero pressure are summarized in Table 25. The thermometer used for all measurements was that described on page 61. The bath employed was No. 2 (page 9).

Table 25

Experimental Data for the Determination of the Dissociation Vapor Pressure and of the Saturated Solution Vapor Pressure.

System	Vol.[a] of reaction flask	Cuprous Halide taken	
	ml.	g.	mmole.
CuCl 2-Butyne	72.7	2.2919	23.143
CuBr 2-Butyne	96.2	2.5698	17.909
CuCl 2-Pentyne	80.5	2.3345	23.574
CuBr 2-Pentyne	72.4	2.8679	19.987
CuCl 3-Hexyne	152.4	2.1979	22.194
CuBr 3-Hexyne	68.7	2.7075	18.869

[a] At zero pressure .

I. DENSITY AND COMPOSITION OF SOLUTIONS SATURATED WITH RESPECT TO THE COMPLEX.

A knowledge of the composition, density, and vapor pressure of solutions saturated with respect to the complex enables one to calculate:

(i) the solubility of the complex,

(ii) the density of the crystalline complex (estimated, and exact, with additional data), and

(iii) the molecular weight of the complex in solution.

The solubilities of cuprous chloride- and cuprous bromide-complexes in the alkynes of interest were determined at 25° under oxygen-free conditions. In addition the solubility of cuprous chloride in 3-hexyne at 19.94° was determined under similar conditions. Densities were measured simultaneously.

The results are summarized in Table 26 which gives the solubility of the cuprous halide in terms of weight and mole percent. Although this is a convenient and unambigous method of data presentation the reader is reminded that in each case (except for cuprous iodide) the saturated solution was in equilibrium with the crystalline complex.

Results. It is interesting to note that for each alkyne mole-percent-wise the cuprous bromide-complex is less soluble than that of the chloride. Though this roughly parallels the dissociation vapor pressure at 25° there is no correlation with the heat of dissociation (Table 19) or the decomposition temperature, T_d (Table 21). Similarly the difference of solubility of the cuprous halide with each alkyne cannot be related to T_r (Table 22). Indeed, the solubility of a molecular complex in excess ligand is not directly related to the stability of the complex (40). However, as explained above (page 104) the actual decomposition temperature of the complex will be related to the solubility at that temperature or, more precisely, to the vapor pressure of the saturated solution at that temperature.

Table 26

Density and Composition of Saturated Solutions at 25°.

Alkyne	Cuprous Chloride			Cuprous Bromide		
	d^{25}_4	wt.%	mole%	d^{25}_4	wt.%	mole%
2-Butyne	0.878	23.89	14.64	0.706	3.81	1.47
2-Pentyne	1.340	52.91	43.59	1.288	49.95	32.18
3-Hexyne	1.090	38.10	33.80	0.888	21.15	13.31
3-Hexyne*	1.013	32.51	28.55			
	Cuprous Iodide					
3-Hexyne	0.717	<0.05	<0.03			

* T = 19.94°

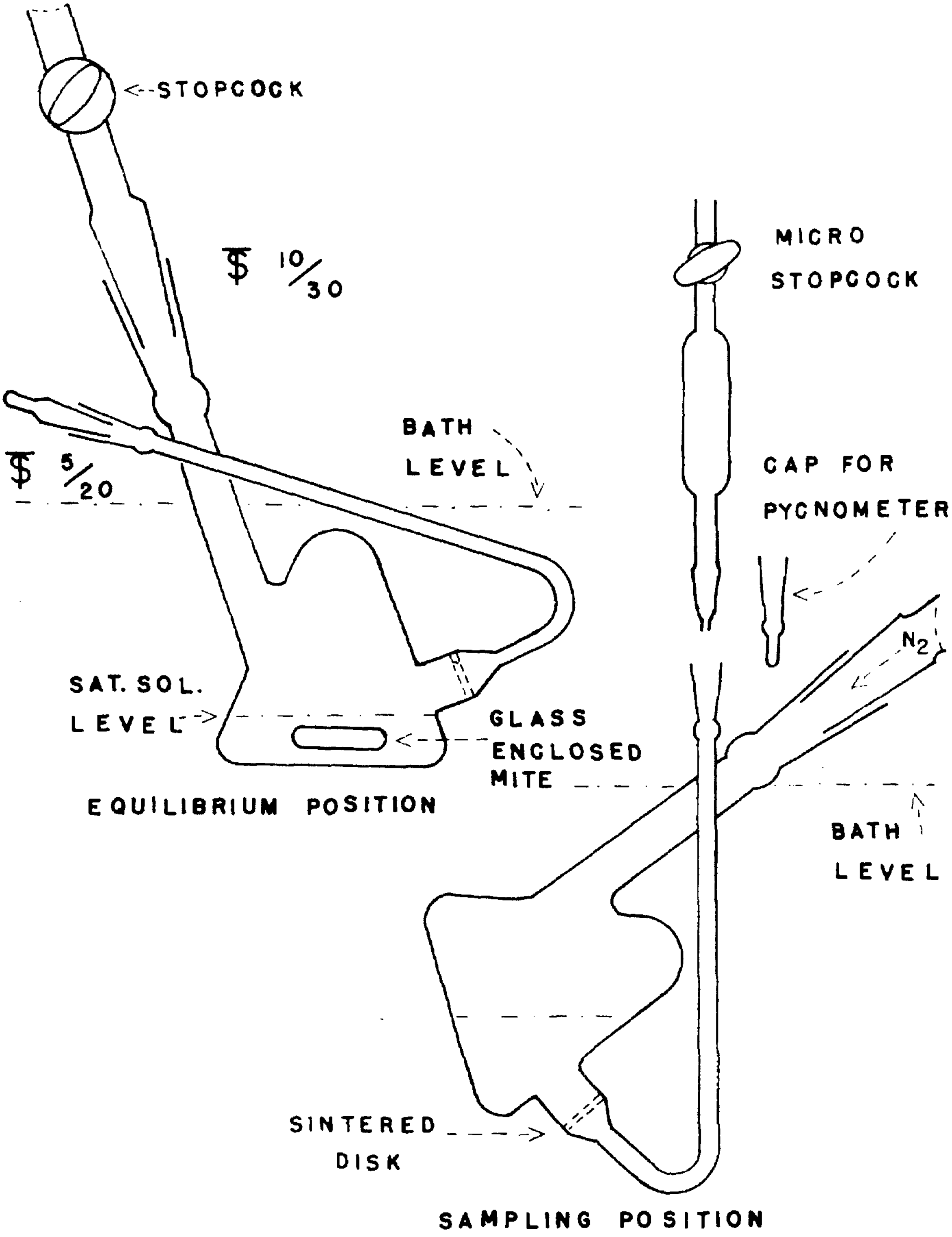
The range of solubilities (1.47 to 43.59 mole percent) is surprisingly large, especially if the complex as such is assumed to exist in solution. If this were the case for cuprous chloride-2-pentyne and cuprous bromide-2-pentyne, one would speak of a saturated solution of 77.4 and 47.5 mole percent complex respectively. Perhaps in the former case one should talk of a solution of 2-pentyne (solute) (22.6 mole percent) in the melted complex. The high solubilities indicate that if the heats of fusion were comparable, then the melting points of the pentyne-complexes and the cuprous chloride-3-hexyne complex would be lower than the melting points of the other complexes. This appears to be the case for the cuprous chloride-2-pentyne and the cuprous chloride-3-hexyne complexes whose melting points are approximately 35.6° and 40.6° respectively. All the other complexes considered here decompose in the melting point apparatus above 40.6° when bulb "B" is at 25°.

The solubility of cuprous iodide in 3-hexyne is so low (less than .03 mole percent) that it cannot be suitably studied by the present method. Furthermore the case was somewhat complicated by air leaking into the equilibration flask. The material recovered from solution and weighed was shown by microscopic examination to be a pale green liquid soluble in acetone and not a buff cuprous iodide. Hence, the actual solubility of cuprous iodide is considered to be much lower than that indicated in Table 26.

The saturated solutions of cuprous halide in 2-pentyne were very viscous, so much so, that even with a coarse sintered disk the time required for the filling of the pycnometer was about two minutes. Thus, although the densities agree within the limit given in Table 26, it might be expected that the density of these solutions at 25° would be somewhat greater. Ambient temperature was about 26.5°.

Experimental Procedure and Details. Cuprous halide (2 - 3 g.) was introduced into the equilibrium flask (Fig. 35) by means of a funnel placed through the standard taper 10/30 joint. An adapter equipped with a stopcock (partially shown in Fig. 35) was fitted into the standard taper 10/30 joint, and the equilibration flask evacuated and degassed over night. The standard taper joint and the stopcock were greased carefully to avoid excess with Dow Corning high vacuum siliconegrease. Alkyne was then distilled into the flask and the cuprous halide was dissolved with the aid of the magnetic stirrer. A careful balance of salt and ligand was necessary in order to have sufficient saturated solution in contact with crystalline complex at 25°. The alkyne was removed and added by distillation. In the problematic cases of the 2-pentyne solutions this balance was achieved with the help of a detachable inverted "U" (comparable to that shown in Fig. 29) which was connected to the equilibration flask and a flask containing pentyne. Two determinations were made in each case.

When the amounts of alkyne had been adjusted in the cases of 3-hexyne and 2-pentyne solutions, nitrogen was



EQUILIBRIUM POSITION

SAMPLING POSITION

Fig. 35 Density and Composition Equilibration Flask and Pycnometer.

added to the flask until the total pressure was one atmosphere. The flasks were equilibrated in bath No. 1 at 25.00 ±0.02° for 3, 6, and approximately 24 hours, respectively, for the 2-butyne, 2-pentyne, and 3-hexyne systems. The great ease of solution and crystallization of all the complexes and the intermittent stirring provided with the underwater stirrer insured that equilibrium had been achieved in the above mentioned times. Care was taken to avoid wetting the sintered disk of the equilibration flask. This was not always realized; however, no crystals were observed in the finally collected saturated solutions.

The pycnometers (two) were fitted with a 5/20 standard taper male joint with the tip pulled down to approximately 1 mm. outside diameter, a female ground glass cap, and a micro-stopcock (see Fig. 35). The micro-stopcock was carefully greased with high vacuum siliconegrease and the excess removed outside and inside. A lint-free pipe cleaner was used to remove the grease inside the bore. Except in the case of the cuprous bromide-2-butyne complex the pycnometer was weighed only after wiping with a damp chamois. In the excepted case the high vapor pressure of the solution at ambient temperature precluded delays of any kind: the pycnometer was cleaned for weighing with a lens tissue.

The tared pycnometers, fitted with a short length of tubing at the outlet of the micro-stopcock prior to use, were stored for one-half hour or more in a large stoppered tube immersed in the water bath. The actual use of the pycnometers was based on the Lucas-Eberz pipette. After the equilibration flask had been placed in the sampling position, the standard taper 5/20 plug removed, and the joint freed of grease, the pycnometer (minus the cap of course) was positioned and nitrogen pressure applied (5-8 lbs./in^2) as indicated in Fig. 35. The saturated solution was forced through the sintered disk up the sampling tube and into the pycnometer. Excess solution was forced through the micro-stopcock and into the tubing fitted at the end. The stopcock was then closed, the pressure released, the pycnometer removed, the tip quickly cleaned with a lens tissue in one motion, the cap replaced on the cleaned tip, and the second pycnometer inserted in the sampling tube. The second pycnometer was then filled in a similar manner. At this point the rubber tubing was removed from the end of the pycnometer. The stopcock end of the pycnometer then thoroughly and quickly cleaned with the aid of several short lengths of pipe cleaner and lens tissue.

After the pycnometers have been weighed a short length of Tygon tubing with a small funnel (15 mm. wide) was attached to the micro-stopcock end. To the funnel was added approximately 1 ml. of alkyne. The cap of the pycnometer was then carefully removed, the stopcock opened, and the saturated solution followed by the "wash" alkyne was allowed to drain into the standard taper 12/30 female joint of a 10-ml.

tared receiver. The tip of the pycnometer was carefully washed off with extra alkyne. The alkyne was removed from the receiver by high vacuum distillation at low temperature. When the residue in the receiver appeared to be only cuprous halide the remaining distillation and decomposition was carried out at ambient temperatures for 24 hours with occasional immersion of the bulb of the receiver into a 400-ml. beaker of hot water. This treatment was repeated until constant weight (receiver) was achieved. The pycnometer was placed in a vacuum desiccator, until constant weight had also been reached. The difference (less than 5 mg.) between the final and the initial weight of the pycnometer was then algebraically added to the weight of the collected residue. The sum represented the weight of the cuprous halide in the sample. The volumes (1.1526 and 1.0517 0.0001 ml.) of the pycnometers were determined with clean mercury at 25.00 ±0.02°.

The recovered cuprous chloride was pure white and the cuprous bromide was tinged a light yellow.

A sintered disk of coarse porosity was used for the determination of solubility of cuprous chloride in 3-hexyne and cuprous chloride and cuprous bromide in 2-pentyne. For the remaining determinations a medium sintered disk was practical since the solutions were much less viscous.

Discussion. Attempts to correlate solubility of a molecular complex in excess ligand with a measure of the stability of the complex should be preceded by discussion considering the heat of solution of the complex in the ligand and the melting point of the complex if:

(i) the solution is in equilibrium with the solid complex, and

(ii) the solubility of the complex increases with the temperature.

If in addition it can be demonstrated that the molecular weight of the material in solution is constant over the temperature range of interest, then it is likely that the solubility of the complex in excess ligand is unrelated to the stability of the complex but is representative of the simpler picture of a solute dissolving in the solvent according to eq. 17, where x represents the mole fraction of the complex in solution and $\Delta h_{soln.}$ is the heat of

$$\frac{d \ln x}{d T}_{sat.} = \frac{\Delta h_{soln.}}{RT^2} \tag{17}$$

solution of the crystalline complex. If the hypothesized supercooled melt of the crystalline complex mixes ideally with the ligand solvent then the heat of solution may be replaced by the heat of fusion (corrected for heat capacity effects). The melting point of the complex, however, may not exist under the pressures at which the gaseous phase of the ligand exists if the decomposition point T_d is low enough. Nevertheless, even if the melting point does not exist, the solution phenomena may be represented by eq. 17.

$$(\mathrm{CuX \cdot Un})_n(\mathrm{solid}) \overset{\mathrm{Un}}{=} (\mathrm{CuX \cdot Un})_n(\mathrm{sat.soln.}) \qquad (18)$$

$$m(\mathrm{CuX \cdot Un})_n(\mathrm{sat.soln.}) = n(\mathrm{CuX \cdot Un})_m\ (\mathrm{soln.}) \qquad (19)$$

$$(\mathrm{CuX \cdot Un})_n(\mathrm{sat.soln.}) - m \cdot n\ \mathrm{Un}(\mathrm{soln.}) = (\mathrm{CuX \cdot mUn})_n(\mathrm{soln.}) \qquad (20)$$

$$(\mathrm{CuX \cdot Un})_n(\mathrm{sat.soln.}) = n(\mathrm{CuX})(\mathrm{soln.}) - n\ \mathrm{Un}(\mathrm{soln.}) \qquad (21)$$

The actual situation in the saturated solution may be complicated by the existence of other species as indicated by eq. 19, 20, and 21. If the heats of reaction for these last three equations are small (either negative or positive) then the solubility (apparent and real) of the complex will increase with rising temperature.

In addition to the above reactions it is known that dissociation of the complex into its constituents near the real decomposition temperature is important. Immediately below this temperature then eq. 21 is important. The distinction between the calculated T_d given for the complexes of this study (Table 21) and T_d' as defined by the reaction of eq. 22 at that temperature resides primarily in the differences of the ligand of their corresponding reactions. For T_d the ligand is pure, whereas for T_d' the ligand is

$$T_d' \qquad \mathrm{CuX \cdot Un}(\mathrm{sat.soln.}) = \mathrm{CuX}(\mathrm{sat.soln.}) + \mathrm{Un}(\mathrm{soln.}) \qquad (22)$$

saturated with respect to the solid complex (CuX·Un) and with respect to the uncomplexed metal constituent (CuX). For complexes not soluble in their ligand (40, 41) T_d

exists and for soluble complexes T'_d exists. It may be here remarked that for temperatures above T'_d the concentration of the species (CuX·Un) in solution is expected to decrease according to the reaction of eq. 23. Hence, if the solubility of CuX as such is small then the apparent solubility of all the cuprous compounds above T'_d will undergo a decline as the temperature increases.

$$\mathrm{CuX{\cdot}Un(soln.)} = \mathrm{CuX(sat.soln.)} + \mathrm{Un(soln.)} \qquad (23)$$

In the present study it has been observed that at room temperature and below the solubility of the complexes increases with rising temperature. Hence, according to the above discussion the melting points and the heats of fusion should be determined and correlated with the solubilities and molecular weights in solution. Deviations from the simplest case considered above would indicate the possibility of reactions like those of 19, 20, and 21.. The extent of the deviation, if present, would be expected to vary according to the alkyne (steric effects) and the halide of the cuprous salt. The bonding capacity of the metal would be expected to vary according to the halide attached and, hence, might be expected to affect the stability of a given species. In the creation of complex species involving severe deformation or breaking of cuprous halide bonds it will be appreciated that the heat of reaction will depend strongly on the halide.

The observation that certain complexes are very soluble in their ligand suggests that certain aspects of the complex in solution have similarities to the solvent. A model of the complex in solution readily follows from these suspected similarities. Comyns (24) found the solubility of silver perchlorate (salt) in a non-polar alkyne (3-hexyne) to be 32 percent at 27°. At a lower temperature a crystalline complex was observed. In this case then what are the similarities (surmised above) of the complex in solution to the ligand 3-hexyne? The same question may be asked concerning the soluble complexes of the present study. The author suggests that the following model may be representative of some complex systems: the complex in solution consists of a nucleus of the inorganic reagent effectively surrounded by complexed ligand. The nucleus is considered neutral and may consist of several molecules of the inorganic component bound together by covalent and possibly ionic or dipolar bonds. Ligand molecules are attached to the outside of the nucleus primarily by bonding with the metal components. Hence, though the inside of the nucleus may be polar, the surface of the nucleus appears to the approaching solvent molecule quite similar to a large hydrocarbon.

For the soluble cuprous halide-alkyne complexes the nucleus components are probably bound together by covalent bonds with the halogen serving as a bridge between two copper atoms. The bridging capacity of halogens is known (42) as is the tendency of copper(ous) atoms to expand their valency to accommodate the presence of more than one halogen atom (43).

An extension of the 'nucleus' model to soluble complexes containing more ionic inorganic constituents such as silver nitrate and perchlorate involves some hazard as a solution of the 'nucleus' complexes would be non-conducting. Vapor pressure measurements of Comyns (40) on a 2-pentyne solution containing 13 percent silver perchlorate indicate that Raoult's law was not obeyed; no vapor pressure lowering was observed, 3.2 mm. was expected. This suggests that the silver perchlorate species or the complexes are highly associated in solution.

In a more polar medium the 'nucleus' complex could be expected to adopt a more polar exterior by dissociation or rearrangement as indicated in eq. 19, 20, and 21. Comyns has observed an increased solubility of the silver nitrate-3-hexyne complex in a mixture of the alkyne and acetone over its solubility in the pure alkyne.

If the 'nucleus' model is applicable to the crystalline complex the van der Waals forces per complexed ligand would be expected to change for various ligands in the same order as the van der Waals forces in the crystalline ligand. The total van der Waals forces for the crystalline complex will however, depend upon the number of complex ligand molecules per molecular complex and, hence, upon the size of the nucleus. Since not all the metal ions or atoms may be binding ligand molecules, but may be submerged in the nucleus, the van der Waals forces for the complex molecules will vary according to the composition of the complex, and will increase with the mole percentage of the inorganic component.

Solomon (44) has correlated the melting points of the olefin-silver nitrate complexes with two factors:

(i) the melting point of the original hydrocarbon and

(ii) the silver nitrate content of the complex.

Although this evidence supports the above model, it is certainly not conclusive and probably has only heuristic value.

The author does not suggest that all alkyne complexes are of the postulated nucleus type. The failure of the complex to be soluble in excess ligand may indicate, when the melting point is low, that the complex is not of the nucleus type (41). The crystal structure of silver perchlorate-dioxane complex (45) (120° decom.) and its very low solubility in dioxane indicates that the stability of the complex depends in part on the cooperative phenomenon of the crystalline state. In this case the silver ions are separated from the perchlorate anions.

J. DENSITY OF THE CRYSTALLINE CUPROUS CHLORIDE-2-BUTYNE COMPLEX AT 25°.

The density of the cuprous chloride-2-butyne complex in the crystalline state was determined by an indirect method in the presence of its mother liquor. Selective solution of 2-butyne by liquids ordinarily used for density determinations would partially destroy the crystals and precipitate cuprous chloride. Practices necessary to avoid decomposition in the liquids preclude the use of common methods of density determination of crystalline materials. In addition the high volatility of 2-butyne (b.p.26.9°) indicates that special techniques are required.

Calculation of d_c. Consider a volumetric flask which contains approximately one-half of its volume of crystals and the remaining half of solution in equilibrium with the crystals. The density of the crystals, d_c, can then be expressed in terms of the density of the mixture, d_T, density of saturated solution, d_s, and w_c/w_T, the weight of the crystals divided by the total weight, as in eq. 24, derivable from the definitions of density and total weight.

$$d_c = \frac{w_c/w_T}{1/d_c - (1-w_c/w_T)/d_s} \qquad (24)$$

The density of the mixture d_T is sum of the weights (w_T) of the two components divided by the volume of the solution plus the volume of the crystalline complex.

Eq. 25 expresses w_T in terms Un_T, the total weight of

$$w_T = Un_T + Cu_T \tag{25}$$

2-butyne and Cu_T, the total weight of cuprous chloride.

The ratio w_c/w_T can be determined at equilibrium from a knowledge of the composition of the phases and the total weights of the two components, Un_T and Cu_T. The weight of the crystals, w_c, is calculated with the aid of eq. 26, where S is the ratio in the liquid phase of the

$$w_c = (1 + C)(Cu_T - (Un_T - C \cdot Cu_T)/(S - C)) \tag{26}$$

weight of 2-butyne to the weight of cuprous chloride and C is the corresponding ratio in the crystalline phase.

Method. The method to obtain d_T and w_c/w_T can be outlined simply as follows: a known weight of 2-butyne is condensed into a volumetric flask containing a weighed amount of cuprous chloride. The reactants are stirred or shaken until all the cuprous chloride is dissolved and the crystalline complex is evident. Equilibration is then allowed to take place at a known temperature and the total volume occupied by the saturated solution and the solid adduct is determined.

Results. Values of d_c have been calculated on the assumption that d_s, S, and C have the values 0.878 g./ml., 3.186 (see Table 26) and 0.5462 (see Table 11) respectively. The data of three successful trials are summarized in Table 27 along with the density of the crystalline complex as determined by an x-ray investigation (see page 187).

Table 27

Density of the Crystalline Cuprous Chloride-2-Butyne Complex at 25°.

Ex.	Total Volume ml.	Total CuCl(Cu_T) g.	Total 2-Butyne(Un_T) g.	d_c g./ml.
1	12.453 ±0.002	6.2338	8.0943	1.730 ±0.003
2	12.262	5.5960	8.0041	1.730
3	12.512	5.6295	8.1724	1.730
x-ray (at 27.0 ±0.5°)				1.727 0.006

<u>Experimental</u> <u>Details</u>. To the top of a 10-ml. Erlenmeyer flask was sealed a 0.2-ml. section of a 1-ml. red line pyrex pipette graduated in 0.01 ml.. A side arm near the bottom of the Erlenmeyer was used for the introduction of a glass enclosed stirrer mite. The apparatus was joined to a high vacuum system by means of a male member of a standard taper 10/30 joint as shown in Fig. 36. Cuprous chloride was introduced into the dry clean tared vessel through the stem. The cuprous chloride was removed from the stem by means of a lint-free pipe cleaner and the vessel was then reweighed and the cuprous chloride added noted. The vessel was then attached to a high vacuum system and evacuated for an hour. Sufficient 2-butyne was then distilled into the vessel to react with all of the cuprous chloride to form a solid complex and that amount of saturated solution which filled the vessel within the limits of volume that could be

measured. This means that the volume of 2-butyne added was estimated correctly within ±0.1 ml.. The estimate, of course, is known to be correct only when the final equilibrium is achieved.

The vessel was then sealed under vacuum above the section of graduated pipette at the place indicated in Fig.36, and the male member of the standard taper 10/30 joint removed. During this process it was necessary to protect the joint from heat; this was accomplished by wrapping the joint with asbestos tape and making the seal as quickly as possible. The weight of the total 2-butyne added was then calculated when the removed male member of the joint was cleaned and weighed with the sealed vessel. The buoyant effect of the air must be taken into account.

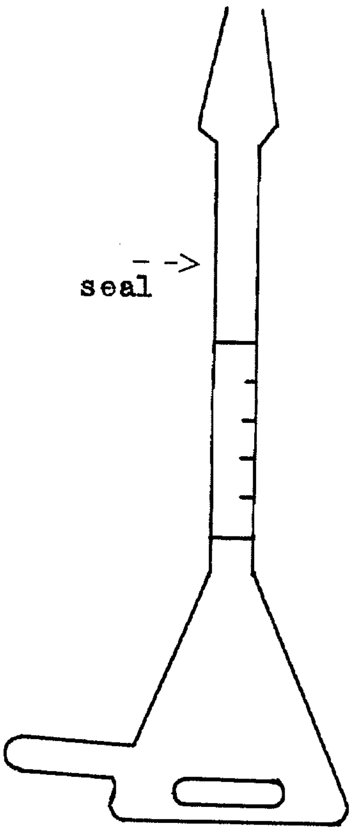


Fig.36
Pycnometer.

Solution of the cuprous chloride was accomplished with the aid of a magnetic stirrer and with gentle heating. In every case it was possible to obtain at greater than ambient temperatures a clear solution without solids present. This condition insured that all of the cuprous chloride had reacted. Colorless crystalline material immediately appeared upon cooling at 25°. The quantity of solid material prevented the use of the magnetic stirrer in the final stages of equilibration. Some stirring was obtained by manual rotation of the inclined vessel in the constant temperature bath several times a day. No change was observed in the height of the saturated solution after the first few hours. One case was observed for seven days. No case was observed for less than 40 hours. A telescope was used to make the readings.

The volume of the flask at the lowest useable 0.1 ml. graduation was determined with mercury at 25° as 12.351 ± 0.001 ml. (average of 12.3508 and 12.3514 ml.).

K. ESTIMATED DENSITIES OF THE CRYSTALLINE COMPLEXES.

From a knowledge of the density and composition of the saturated phases it has been possible to make reasonable estimates of the densities of the crystalline complexes. These estimates should prove useful in crystal structure investigations.

Results. In Table 28 are given the density of the crystalline complex $d_{c_{M.V.}}$, as calculated from the molecular volume of the pure alkyne and of the pure cuprous halide; the density of the crystalline complex, $d_{c_{soln.}}$, as calculated from the density and composition of the saturated solution; the approximate volume change, Δv, of formation of one mole of crystalline complex from pure solid cuprous halide and pure liquid alkyne; and the

Table 28

Estimated Density of the Crystalline Complexes at 25° and the Data used.

Complex	$d_{c_{M.V.}}$ g./ml.	$d_{c_{soln.}}$ g./ml.		Δv ml./mole	$d_{c_{est.}}$ g./ml.
CuCl-2-Butyne	1.43	1.68	0.01	16.0	1.73
CuCl-2-Butyne	1.43	(1.730	0.003)[a]	18.3	(1.73)[a]
CuCl-2-Pentyne	1.34	1.50	0.01	13.3	1.53
CuCl-3-Hexyne	1.27	1.41	0.01	13.5	1.43
CuCl-3-Hexyne	1.28	1.40	0.01*	11.9	1.53
CuBr-2-Butyne	1.81	1.52	0.4	-20.7	2.06
CuBr-2-Pentyne	1.67	1.83	0.01	11.0	1.86
CuBr-3-Hexyne	1.56	1.69	0.01	10.9	1.72

[a] d_c, determined by an indirect pycnometric method, see Table 27.

* T = 19.94°.

estimated density, $d_{c_{est.}}$, of the crystalline complex.

Calculation of $d_{c_{M.V.}}$, $d_{c_{soln.}}$ and Δ v. The density of the pure alkynes at 25° were those given on pages 62, 63, and 64 and the density of 3-hexyne at 20° was that given by Pomerantz et al. (34) (0.7226 g./ml.). The density of cuprous chloride (3.53 g./ml.) and cuprous bromide (4.72 g./ml.) at 20° (46) were also used in the calculation of $d_{c_{M.V.}}$.

In addition to the knowledge of the density and composition of the saturated phases two rather unlikely assumptions were made in order to make the calculation of $d_{c_{soln.}}$;

(i) the complex in solution is of the form $(CuX \cdot Un)_n$ and

(ii) the molecular volume of the alkyne and of the supercooled melted complex are additive.

The densities of the saturated solutions are given in Table 26. Compositions of the solutions were recalculated according to the assumption (i) where n = 1. The calculated densities of the complexes, $d_{c_{soln.}}$, are those of the liquid complexes, in view of assumptions (i) and (ii).

For the calculation of Δ v the molecular volume of the crystalline complex is calculated from $d_{c_{soln.}}$.

Calculation of $d_{c_{est.}}$. With the increasing molecular weight of the alkyne, the value of $d_{c_{M.V.}}$ is seen to rise steadily for each cuprous halide. The increase is parallelled by the density ($d_{c_{soln.}}$) as determined from the solubility measurements except that the increase for the cuprous chloride-2-butyne complex is somewhat greater than that for the other members of either series. This deviation is, of course, also reflected in the molecular volume difference column. The noticeable exception to this parallelism is $d_{c_{soln.}}$ for the cuprous bromide-2-butyne complex. However, because of the much lower solubility of the complex, the percentage error is greatly magnified in calculation. This exception is not considered significant.

The agreement of the crystalline densities for the cuprous chloride-3-hexyne complex at 20° and 25° is satisfying considering the assumptions. This adds a measure of confidence in the results of the calculations. The densities of the crystalline cuprous chloride-2-butyne complex, measured by other methods (see Table 27) are in remarkable agreement with that calculated from the solubility determinations. The difference in densities might be ascribed to that between a crystalline and liquid state, although it is somewhat less (by about 1/2 to 1/3) than that usually found for organic compounds (47). This difference in terms of the molecular volume is subtracted from the molecular volume of the crystalline complex calculated from $d_{c_{soln.}}$ in order to obtain the estimated crystalline complex density $d_{c_{est.}}$. For cuprous chloride-2-butyne complex the value 2.06 g./ml. is estimated from the expected parallelism between the densities of the chloride and bromide complexes.

L. VAPOR PRESSURE OF SATURATED SOLUTIONS.

For the six systems studied the vapor pressures of the alkyne solutions saturated with complex at 25° have been measured. In addition the vapor pressure of the saturated solution for the cuprous chloride 3-hexyne system has been determined as a function of temperature from 5.2° to 35.0°.

Results: Saturated Solutions at 25°. In Table 29 are summarized the measured vapor pressure of the saturated solution, P_s, at 25°; the pressure difference $\Delta P = (P_o - P_s)$ between the pressure of the pure alkyne at 25°, P_o, and the pressure of the saturated solution; the ratio $\Delta P/P_o$; the formal mole fraction of cuprous chloride, x_{CuX}, in the saturated solution; n', the ratio of the total moles of alkyne in the non-gaseous phases to the total moles of the cuprous halide present; and N/γ'. The vapor pressures of the saturated solutions for the different values of n' agree within the limits given. The vapor pressure of the saturated solutions, P_s, and the pressure difference, ΔP, for the cuprous chloride 3-hexyne system were obtained by interpolation from data at other temperatures.

Discussion. Raoult's law for the vapor pressure lowering of a volatile solvent by non-volatile solute is eq.27, where

$$\frac{\Delta P}{P_o} = x(\text{solute}) \qquad (27)$$

x is the mole fraction of the solute species in solution. For non-dilute solutions and for cases where the species in

Table 29

Saturated Solution Vapor Pressure Data at 25°.

System	P_s mm.		ΔP mm.		$\frac{\Delta P}{P_o}$	x_{CuX}	n'	$\frac{N}{\gamma'}$	
CuCl 2-Butyne	673.1	±0.3	34.7	±0.6	0.049	0.1464	2.272 1.977	2.99	±0.002
CuCl 2-Pentyne	120.6	0.8	116.4	0.1	0.491	0.4359	1.289 1.216	0.888	0.008
CuCl 3-Hexyne	68.8	0.3	16.5	0.6	0.194	0.3380	1.2	1.75	0.02
CuCl 3-Hexyne*	58.5	0.3	8.0	0.6	0.120	0.2855	1.2	2.38	0.03
CuBr 2-Butyne	704.0	0.5	3.8	0.8	0.005	0.0147	3.661 2.697	2.7	0.6
CuBr 2-Pentyne	192.5	0.7	44.5	1.0	0.188	0.3218	2.090 1.801 1.887	1.72	0.04
CuBr 3-Hexyne	83.4	0.3	1.7	0.6	0.020	0.1331	3.252 2.848	6.7	2.3

* T = 19.94°

solution is not known eq. 27 may be modified for the purpose of this discussion to eq. 28, where x_{CuX} is the

$$\frac{\Delta P}{P_o} = \frac{\gamma' x_{CuX}}{N} \qquad (28)$$

formal mole fraction of cuprous halide in solution, x_{CuX}/N is the sum of the mole fraction of all species in solution containing cuprous halide (eq. 29), and γ' is an 'average' activity coefficient. It will be noted that N is a

$$\frac{x_{CuX}}{N} = \sum_{\text{all } i} x_i (\text{species containing CuX in soln.}) \qquad (29)$$

measure of association of cuprous halide in solution. Even for a single species in solution γ' is not the customary activity coefficient introduced by Lewis (48); hence, $\gamma' \cdot x(\text{solute})$ is not the activity of the solute. Eq. 28 above defines γ'. For dilute solutions γ' approaches the value of the customary activity coefficient for a single species. The ratio N/γ' in Table 29 is simply $P_o\, x_{CuX}/\Delta P$.

For the cuprous bromide 2-butyne system for which Raoult's law would be expected to hold $N/\gamma' \cong N = 2.7 \pm 0.6$. This suggests that the average complex in this solution was a trimer. Other saturated solutions, for which some deviation from Raoult's law may be expected, also indicate association. If, for the more concentrated solutions, as of the cuprous chloride 2-pentyne, cuprous bromide 2-pentyne, and cuprous chloride 3-hexyne systems, x_{CuX}

is replaced by $x_{CuX \cdot Un}$, assuming a 1-to-1 complex, the N/γ' values are 1.58, 2.52, 2.62 (at 25° for cuprous chloride 3-hexyne), and 3.34 (at 19.94° for cuprous chloride 3-hexyne). The general conclusion could be drawn that in solution the complexes exist as polymers were it not for the fact that the values of γ' for the systems having concentrated saturated solutions are unknown and might be considerably different from unity. This conclusion, coupled with the agreement of the estimated density with the measured density of the cuprous chloride-2-butyne crystalline complex would lend support to the nucleus model of the complexes in solution for the systems described here.

The Vapor Pressure of the Saturated Solution, P_s, of the Cuprous Chloride 3-Hexyne System as a Function of Temperature. An interesting example of the thermodynamic conditions accompanying the decomposition of the crystalline complexes soluble in excess ligand is afforded by the cuprous chloride 3-hexyne system. The distinction between P_d and P_d' was manifested by this case.

Theoretical Considerations. As is often the case, there is some pedagogical merit in considering a simplified example for comparison to the problem at hand.

Consider the variation of vapor pressure of a saturated solution, P_s, as a function of temperature. As the temperature increases the vapor pressure of the pure liquid P_o

increases exponentially. However, for a saturated solution the vapor pressure is depressed due to the presence of the solute. Moreover the amount of depression increases as the temperature rises since more solute enters the solution.

The equilibrium between the vapor phase, the solution, and the crystalline solute will be considered. For the solvent, designated by the subscript h, the chemical potential μ_h at equilibrium will be the same for the gaseous and liquid phases as in eq. 30, where the superscripts

$$\mu_h^g = \mu_h^l \tag{30}$$

refer to the gaseous and liquid states. For a small change in temperature a new set of equilibrium states exist as indicated in eq. 31. Whence eq. 32 follows upon comparing eq. 31 with eq. 30.

$$\mu_h^g + d\mu_h^g = \mu_h^l + d\mu_h^l \tag{31}$$

$$d\mu_h^g = d\mu_h^g \tag{32}$$

Eq. 33 is the result of expanding the total differentials in terms of the partial differentials of the chemical potential

$$\left(\frac{\partial \mu_h^g}{\partial P}\right)_{T,A_h} dP + \left(\frac{\partial \mu_h^g}{\partial T}\right)_{P,A_h} dT = \left(\frac{\partial \mu_h^l}{\partial P}\right)_{T,A_h} dP + \left(\frac{\partial \mu_h^l}{\partial T}\right)_{P,A_h} dT + \left(\frac{\partial \mu_h^l}{\partial A_h}\right)_{P,T} dA_h \tag{33}$$

$$v^g dP - s^g\, dT = v^l\, dP - s^l\, dT + RT\, d\ln A_h \tag{34}$$

with respect to the relevant variables. Substitution of the partial differentials with the appropriate partial molar quantities in eq. 33 gives eq. 34 where the subscript h is dropped from most of the partial molar quantities and where A_h is the activity of the solvent, v is the partial molar volume, and s is the partial molar entropy. Collecting terms and considering $P_s = P =$ fugacity (solute assumed to be non-volatile) eq. 34 can be written as eq. 35. This

$$(v^g - v^l)\ d\ P_s - (s^g - s^l)\ d\ T = RT\ d\ \ln A_h \tag{35}$$

equation can be further simplified to eq. 36 if $(s^g - s^l)$ is replaced by $(h^g - h^l)/T$ and if it is assumed that $v^g \gg v^l$ and $v^g = RT/P$, where h refers to the partial molar enthalpy of the appropriate states. However, $(h^g - h^l)$ is the heat of

$$\frac{RT}{P}\ dP - \frac{h^g - h^l}{T}\ dT = RT\ d\ \ln A_h \tag{36}$$

vaporization for the pure solvent. Eq. 37 is obtained upon inserting $\Delta h_{vap.}$ and rearranging eq. 36.

$$d\ \ln P - d\ \ln A_h = \frac{\Delta h_{vap.}}{RT^2}\ d\ T \tag{37}$$

For the solute eq. 38 is well known where the subscript

$$(v_S^l - v_S^s)\ d\ P + RT\ d\ \ln A_S = \frac{\Delta h_{fus.}}{T}\ d\ T \tag{38}$$

S refers to the solute and the superscript s to its pure crystalline phase, A_S to its activity in solution and $\Delta h_{fus.}$ to its heat of fusion. For the purposes of this discussion the $(v_S^l - v_S^s)$ d P term may be neglected as small. When eq. 38 is rearranged and then added to eq. 37, upon collecting terms, eq. 39 results. If the heat capacity

$$d \ln \frac{P A_S}{A_h} = \frac{\Delta h_{vap.} + \Delta h_{fus.}}{RT^2} d T \qquad (39)$$

effects are ignored eq. 39 may be simply integrated to form eq. 40. P, however, is the vapor pressure of the saturated

$$\ln \frac{P A_S}{A_h} = - \frac{\Delta h_{vap.} + \Delta h_{fus.}}{R} \left(\frac{1}{T}\right) + C \qquad (40)$$

solution, P_s, and $A_h = P_s/P_o$ so that eq. 40 can be written as eq. 41. If the assumption is made that the solution is

$$\ln P_o A_S = - \frac{\Delta h_{vap.} + \Delta h_{fus.}}{R} \left(\frac{1}{T}\right) + C \qquad (41)$$

an ideal binary mixture then Raoult's law is expected to hold in eq. 42, where x_S is the mole fraction of the solute.

$$A_S = x_S = \frac{P_o - P_s}{P_o} \qquad (42)$$

When this substitution is made a particularly simple relation between the vapor pressure lowering and the temperature is given, namely eq. 43.

$$\ln (P_o - P_s) = - \frac{\Delta h_{vap.} + \Delta h_{fus.}}{R} \left(\frac{1}{T}\right) + C \qquad (43)$$

It is interesting to note that for a given change in temperature the vapor pressure lowering ΔP increases at a greater rate than does the vapor pressure of the pure solvent P_s. The $\Delta h_{fus.}$ term is responsible for this distinction.

Hence, it is to be expected that for the ideal case the vapor pressure of the saturated solution will pass through a maximum at some temperature T_m, and that thereafter a decrease in P_s will accompany any further increase in temperature. Another condition holding at T_m for the ideal case is eq. 44 from which follows eq. 45.

$$T_m \qquad \frac{d\ P_s}{d\ T} = \frac{P_s}{RT^2}\ (\Delta h_{vap.} - \frac{P_o - P_s}{P_o} \Delta h_{fus.}) = 0 \qquad (44)$$

$$T_m \qquad \Delta h_{vap.} = \frac{P_o - P_s}{P_o}\ \Delta h_{fus.} \qquad (45)$$

<u>Experimental</u> <u>Results</u>. The interesting features of the above model are exhibited by the cuprous chloride 3-hexyne system. P_s, the vapor pressure of the saturated solution, passes through a maximum as shown by the curve AB in Fig.37. At A (5.2°) the vapor pressure of the saturated solution is very close to that of the pure hexyne. However, as the temperature rises $(P_o - P_s)$ increases. The vapor pressure of the saturated solution P_s increases until T_m (31.1°) where P_s is a maximum (57.1 mm.), thereafter P_s decreases. At B, however, all the crystalline complex had been dissolved ($n = 1.190$). If more complex had been present, that is to say, if n, the ratio of the total moles of 3-hexyne to the moles of cuprous chloride, had been closer to unity, then P_s would have continued downward to P_d' as the temperature increased. However, at B the vapor pressure of the solution

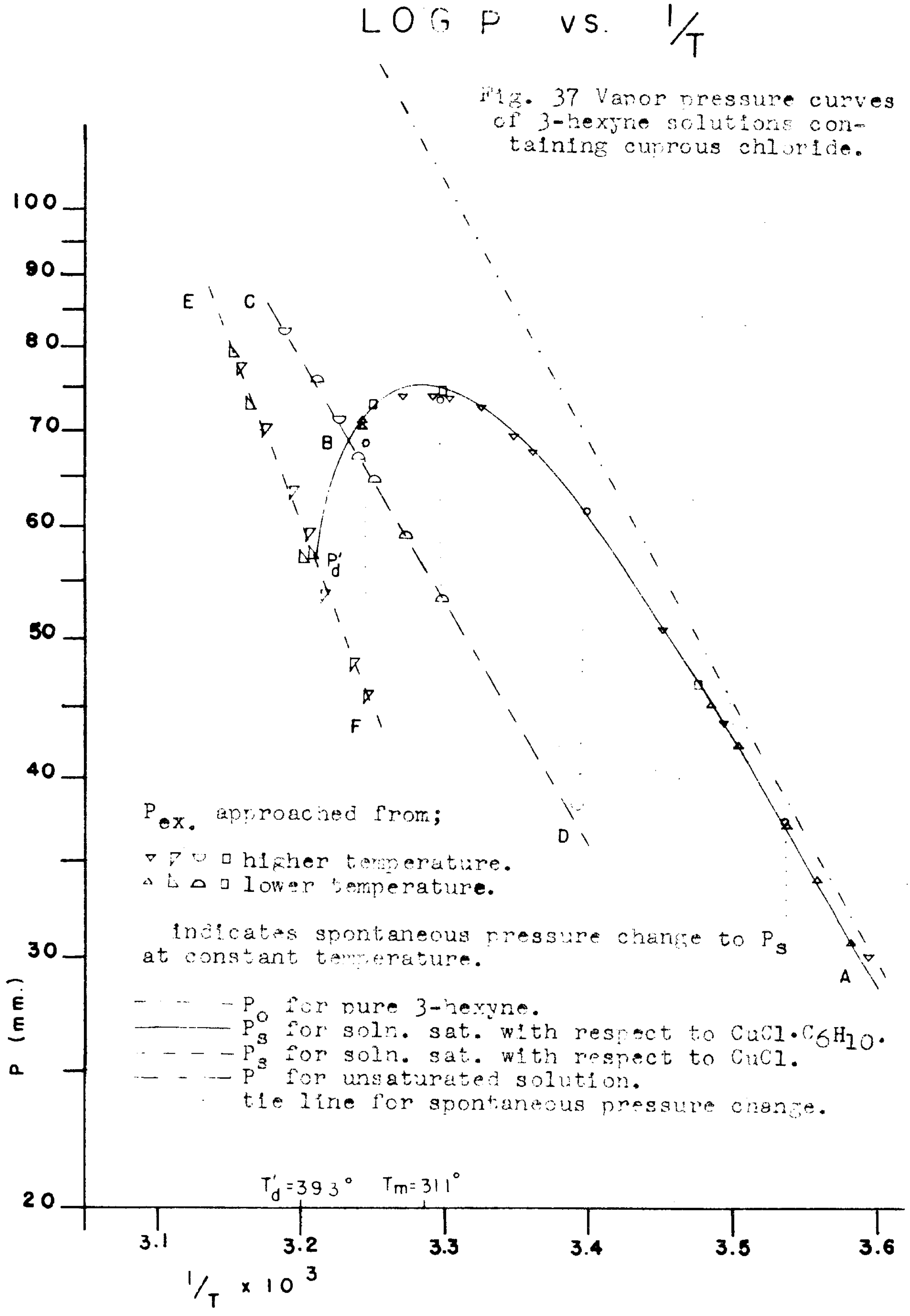


Fig. 37 Vapor pressure curves of 3-hexyne solutions containing cuprous chloride.

(no longer saturated) actually increased toward C. This solution could be supercooled as indicated by the line BD. When crystallization finally occurred (in one to 15 hours after attainment of pseudo-equilibrium) the vapor pressure increased to the vapor pressure of the saturated solution, P_s, as indicated in Fig. 37.

The experimental values of P_s, after crystallization occurred, are given in Table 30 and are indicated by S in the approach column.

When n was reduced to 0.954 and the system warmed carefully to 44° (Ex.51, Table 31) the crystalline complex (still present at 37.7°) melted or dissolved at about 39.3° with the formation of a white precipitate and a solution. This is indicated as P_d' on Fig. 37 and corresponds to T_d'.

An ampoule containing 0.53 g. of 3-hexyne and 0.56 g. of cuprous chloride ($n = 1.14$), when warmed to 44.0 ±0.5° similarly gave a white solid. When this solid was removed from the ampoule and observed microscopically on a micro-hot-stage melting point apparatus no change occurred up to 320°. Hence, it was surmised that the solid was cuprous chloride.

Therefore it is assumed that at T_d' the reaction of eq. 22 was taking place. Above T_d' the pressure percentage increases rapidly and as indicated by eq. 46 more rapidly than for the pure alkyne (compare 12.0 Kcal./mole with

Table 30

Vapor Pressure Data for 3-Hexyne Solutions Saturated with Respect to the Cuprous Chloride-3-Hexyne Complex.

Ex.	Equi. Time hrs.	T °C	$P_{s_{ex.}}$ mm.	$(P_o-P_s)_{ex.}$ mm.	$(P_o-P_s)_{cal.}$ mm.	Approach
1	24	27.31	72.5	22.8	22.9	A
2	22	29.92	74.5	33.2	33.0	B
3	22	29.92	74.6	33.1	33.0	A
4	28	33.92	73.0	56.6	56.7	B
7	7	34.97	71.3	64.7	65.3	B
8	24	33.92	72.9	56.7	56.7	A
9	23	32.32	73.9	46.5	45.7	A
10	29	30.33	74.1	35.8	43.9	A
11	48	29.92	74.0	33.8	33.0	A
12	25	25.44	69.3	17.8	17.6	A
13	33	24.36	67.7	15.0	15.1	A
14	26	35.13	70.9	66.0	66.6	B
20	18	29.72	73.7	33.0	32.0	S
23	23	20.95	61.3	8.6	9.2	S
24	20	16.37	50.7	4.7	4.7	A
25	15	14.36	46.6	3.4	3.4	B
26	3	14.37	46.7	3.3	3.5	A
28	24	9.54	37.2	1.5	1.7	S
30	5	5.92	30.7	1.1	1.1	B
31	24	7.72	34.0	1.1	1.2	B
32	27	9.52	36.9	1.8	1.6	B
33	24	12.12	42.2	2.3	2.4	B
34	26	12.96	43.8	2.7	2.8	A
35	48	13.66	45.0	3.2	3.1	B
29*	25	5.24	30.0	0.7	1.1	A
59*	6	34.72	68.6	65.8	63.1	S

* Only one reading was taken; data not included in least squares treatment.

In the Approach column A means $P_{s_{ex.}}$ was approached from a higher temperature, B means $P_{s_{ex.}}$ was approached from a lower temperature, and S means that the temperature was constant and $P_{s_{ex.}}$ was approached after a spontaneous change of phases.

$$\log(P_o-P_s) = -\,5490.04\left(\frac{1}{T}\right) + 19.631$$

The standard deviations are $\sigma(A) = 0.27$ and $\sigma(C) = 0.093$ (see eq.47).

$\Delta h_{vap.}$ for 3-hexyne, i.e. 8.54 Kcal/mole). This is interpreted as being an example of the reaction of eq. 23

$$T > T'_d \qquad \log P_s = - 2631.76/T \quad 10.199 \qquad (46)$$

(page 129), where less total cuprous chloride is present in solution the higher the temperature. Above P'_d the curve EP'_d represents an equilibrium state, but the curve P'_dF like BD represents a pseudo-equilibrium condition. This will be the subject of a later discussion.

A plot of $\ln(P_o - P_s)$ against the inverse absolute temperature according to eq. 43 gives a straight line (Fig. 38). This is a truly remarkable result in view of the facts that curve AB in Fig. 37 passes through a maximum while in Fig. 38 curve AB is straight and that the solute concentration is very high. The fit of the experimental data to the line is very good. The deviations observed at A (Fig. 38) are within the experimental error. The datum is fitted to a least square curve of the form eq. 47. From the A term according to eq. 43 a $\Delta h_{fus.}$ was calculated to be 16.8 Kcal/mole .

$$\log (P_o - P_s) = A \frac{1}{T} + C \qquad (47)$$

This is, of course, the same as the value calculated from eq. 45 at T_m.

The meaning of $\Delta h_{fus.}$ and the reason for the rectilinearity of the plot is uncertain. The simple model above

LOG $(P_o - P_s)$ vs. 1/T

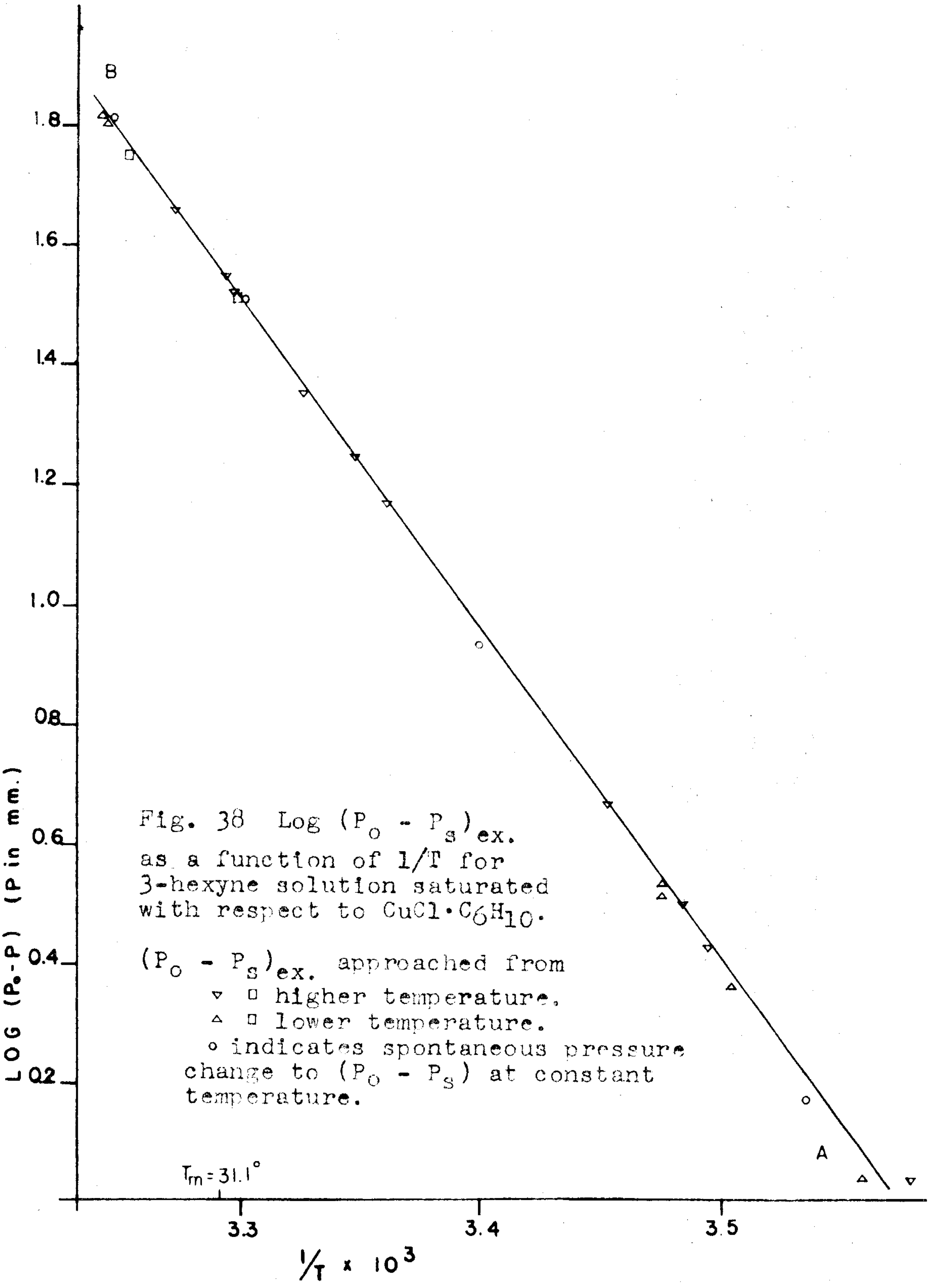


Fig. 38 Log $(P_o - P_s)_{ex.}$ as a function of 1/T for 3-hexyne solution saturated with respect to $CuCl \cdot C_6H_{10}$.

$(P_o - P_s)_{ex.}$ approached from

▽ □ higher temperature,

△ □ lower temperature.

○ indicates spontaneous pressure change to $(P_o - P_s)$ at constant temperature.

suggests that $h_{fus.}$ is the heat of fusion for the crystalline complex and that the solution follows the ideal case. When the composition data of the saturated solution in terms of the mole fraction of the cuprous chloride-3-hexyne complex are extrapolated upwards to T'_d (39.3°) the non-gaseous phase is calculated to be 98 percent complex at that temperature. However, it is known from calculations of N/γ' for cuprous chloride 3-hexyne system at 25° and 19.94° that deviations from ideality do indeed exist. Thus the rectilinearity of Fig. 38 is probably fortuitous, however, a more detailed investigation (especially of composition and molecular weight in solutions at higher temperatures) should prove interesting.

P_o was calculated from the vapor pressure determinations mentioned earlier according to eq. 2 and the values of Table 6. The extrapolated vapor pressure at approximately 35° deviates about 2 mm. from that expected according to the boiling point and other vapor pressure measurements of 3-hexyne at isolated intermediate temperatures (37). This would have a slight effect (one of lowering in pressure the experimental data) at B; only the points above 34° (below 3.25 on the 1/T scale on Fig. 38) would be noticeably affected.

As was mentioned above the supercooled solution of cuprous chloride (curve P'_dF) was not in equilibrium. Since $n = 0.954$, the equilibrium system does not include solutions but only the crystalline complex and the solid cuprous

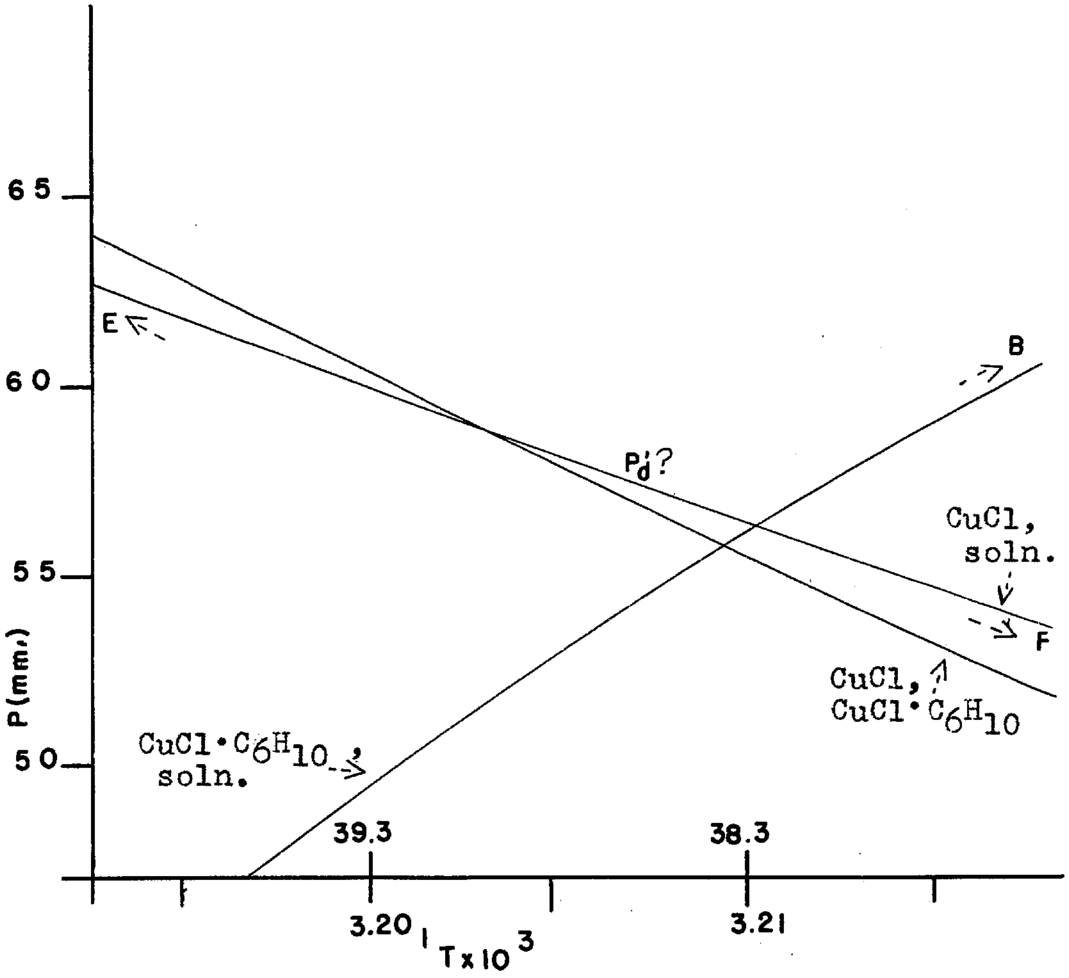


Fig. 39 Vapor Pressure Curves in the Region of T_d' for the Cuprous Chloride 3-Hexyne System.

chloride (besides the vapor phase). This is indicated in Fig. 39. It is seen that below T_d' (39.3°) the cuprous chloride-3-hexyne complex, cuprous chloride system has a lower vapor pressure than the 3-hexyne solution, cuprous chloride system. Hence it might be expected that when crystallization occurs the vapor pressure is lowered to the corresponding P_c. However, in a case observed (Ex.58, Table 31), the vapor pressure actually increased (Ex.59, Table 30), with the formation of the saturated solution. However, this was just an intermediary pseudo-equilibrium state since solid cuprous chloride was present, presumably protected by the crystalline complex.

Thermodynamically the presence of the four phases, cuprous chloride-3-hexyne complex (solid), cuprous chloride (solid), 3-hexyne (solution), 3-hexyne (vapor), and two components would specify a unique equilibrium state. Fig. 39 does not illustrate this however, but instead shows three such unique states. If the crystalline complex in equilibrium with the saturated solution is the same phase as that for which P_c was determined over the temperature range of interest then Fig. 39 is in error. The disparity is not expected to be due to the presence of a new crystalline phase but rather to an error in the extrapolation of curve AB to P'_d.

T'_d is calculated from the simultaneous solution of the least squares curve for P_c (cuprous chloride-3-hexyne complex) and for P_s (saturated with respect to cuprous chloride). T'_d is found to be 39.3° while T_d has been calculated as 66.0° (see Table 21).

The experimental data for the solution saturated with respect to cuprous chloride (curve EP'_dF in Fig. 37) are given in Table 31. These data were fitted to a curve of the form eq. 48 by the method of least squares. The results are indicated in eq. 46 and $P_{s_{cal.}}$ is compared with $P_{s_{ex.}}$ in Table 31.

$$\log P_s = A/T + C \tag{48}$$

<u>Experimental Details.</u> Unless stated to the contrary, each measured vapor pressure $P_{s_{ex.}}$ in Tables 29, 30, and 31 is the average of at least four readings. The equilibrium time of the experimental data in Table 29 was at least one day. The remaining experimental details were the same as those given on page 116 for the dissociation vapor pressure study.

Table 31

Vapor Pressure Data for 3-Hexyne Solutions Saturated with Respect to Solid Cuprous Chloride.

Ex.	Equi. time hrs.	T °C	$P_{s_{ex.}}$ mm.	$P_{s_{cal.}}$ mm.	Approach
51	8	44.13	79.6	79.5	B
52	26	43.5	77.8	77.4	A
53	9	41.7	70.1	69.3	A
54	24	39.97	63.2	62.4	A
55	24	38.85	59.1	58.2	A
56	24	37.52	53.9	53.5	A
57	24	35.62	48.1	41.5	A
60	28	38.36	57.6	56.4	B
66	2	39.17	57.0	59.4	B
67	48	39.15	57.0	59.3	B
68	8	42.83	73.0	74.3	B
58*	6	34.77	45.7	45.0	A

* One reading only; data not included in least squares treatment.

In the Approach column A indicates that the experimental vapor pressure was approached from a higher pressure, B, from a lower pressure.

$$\log P_s = -2631.76\,\frac{1}{T} + 10.199$$

The standard deviations are $\sigma(A) = 2.8$ and $\sigma(C) = 0.28$ (see eq. 48).

M. VAPOR PRESSURE LOWERING AS A FUNCTION OF TEMPERATURE FOR CONSTANT COMPOSITION.

Association of a solute in a dilute solution may be detected by an abnormal lowering of the vapor pressure. For non-dilute solutions it is difficult to interpret the data correctly because of unknown activity coefficients. However, changes in the degree of association with temperature may be detected because in non-ionic media activity coefficients are not strongly temperature dependent.

The vapor pressure difference between the pure alkyne and a non-saturated solution containing cuprous chloride was determined for 2-butyne and 2-pentyne between 19° and 75°. In order to have comparable studies, the mole fraction of the cuprous chloride in each alkyne was about the same (0.1). This concentration was necessary in order to obtain significant measurements for the 2-pentyne system at room temperature. Such a high mole fraction of solute has the additional advantage that whenever dissociation effects are strongly temperature dependent, then the percentage change of the species in solution will be greater than for the more dilute solutions, in which some dissociation has already taken place.

Theoretical. The effect of temperature upon the percentage vapor pressure lowering will be considered in a simple example.

Earlier (page 143) γ'/N is defined by the modified Raoult's law, eq. 28, here called eq. 49. $(P_o - P)/P_o$ is equivalent to $(1 - A_h)$, where A_h is the activity of the solvent

$$\frac{P_o - P}{P_o} = \frac{\gamma'}{N} x_S \tag{49}$$

in the solution. If the percentage vapor pressure lowering is differentiated with respect to temperature, holding the concentration of all the species in solution constant after equating $(1 - A_h)$ to $x_S \cdot \gamma'/N$, eq. 50 follows immediately, where x_h is the mole fraction of the solvent and γ_h is its activity coefficient. The experimental method requires that partial differentiation with respect to temperature is not at constant pressure, eq. 50.

$$\left(\frac{\partial}{\partial T}\left(\frac{P_o - P}{P_o}\right)\right)_x = \frac{x_S}{n}\left(\frac{\partial \gamma'}{\partial T}\right)_x = - x_h\left(\frac{\partial \gamma_h}{\partial T}\right)_x \tag{50}$$

Dividing eq. 50 by the constant x_S and multiplying the right hand term by γ_h/γ_h gives eq. 51.

$$\left(\frac{\partial}{\partial T}\left(\frac{P_o - P}{P_o\, x_S}\right)\right)_x = \frac{1}{n}\left(\frac{\partial \gamma'}{\partial T}\right)_x = - \frac{x_h\, \gamma_h}{x_S}\left(\frac{\partial \ln \gamma_h}{\partial T}\right)_x \tag{51}$$

However, $(\partial \ln \gamma_h / \partial T)_x$ in this equation is given by eq. 52 and 53, where the superscript * refers to the state

$$\left(\frac{\partial \ln \gamma_h}{\partial T}\right)_x = \left(\frac{\partial \ln \gamma_h}{\partial T}\right)_{x,P} + \left(\frac{\partial \ln \gamma_h}{\partial P}\right)_{x,T} \cdot \left(\frac{\partial P}{\partial T}\right)_x \tag{52}$$

$$= - \frac{h - h^*}{RT^2} + \frac{v_h - v_h^*}{RT}\left(\frac{\partial P}{\partial T}\right)_x \tag{53}$$

of the pure solvent. The term $(h-h^*)$ is evidently the partial molar heat of mixing and similarly $(v_h-v_h^*)$ is the partial molar volume change for the solvent upon mixing. As a good approximation for the present experimental cases it may be assumed that eq. 54 holds. Hence,

$$\left(\frac{\partial P}{\partial T}\right)_x = \left(\frac{\partial P_o}{\partial T}\right)_{equil.} = \frac{\Delta h_{vap.}}{RT^2} \qquad (54)$$

when the appropriate substitutions are made, eq. 51 can be rewritten as eq. 55.

$$\left(\frac{\partial}{\partial T}\left(\frac{P_o - P}{P_o\, x_S}\right)\right)_x = -\frac{x_h\ \gamma_h}{x_S}\left(-\frac{h-h^*}{RT^2}+\frac{v_h-v_h^*}{RT}\cdot\frac{\Delta h_{vap.}}{RT^2}\right) \qquad (55)$$

However, since the effect of pressure upon the activity coefficients is usually negligible the furthermost right hand term may be ignored. The heat of mixing for the non-electrolytes, especially for non-polar solvents, may be expected to be small also, hence, eq. 55 simplifies to eq. 56.

$$\left(\frac{\partial}{\partial T}\left(\frac{P_o - P}{P_o\, x_S}\right)\right)_x = \frac{1}{n}\left(\frac{\partial \gamma'}{\partial T}\right)_x = 0 \qquad (56)$$

This indicates that for the cases considered $\left(\frac{P_o - P}{P_o\, x_S}\right)_x$ should be independent of temperature. Therefore large deviations from constancy of γ'/N as a function of temperature must be explained on a basis different from one developed on activity coefficient dependency upon temperature and pressure.

Calculation. In addition to the measured value of (P_o-P)

it is necessary to know P_o as a function of temperature. The large range of temperature precluded an extrapolation of the data for P_o (summarized in Table 6) from being used with assurance. However, for 2-butyne the pressure P_o was calculated from the formula given by Heisig and Davies (Table 6) of the form of eq. 57. For the purpose of calculating P_o for 2-pentyne above 25° the following subterfuge was employed, namely, extrapolating eq. 57 using A as given for 2-pentyne in Table 6, and using constants B and C determined from the boiling point (56.12°) and the known data at 25°.

$$\log P_o = A \frac{1}{T} + B \log T + C \tag{57}$$

The values for B and C were determined as 0.50832 and 8.21456 respectively. P_o, as determined from this method of calculation is estimated to be within a maximum of 2 percent of the actual vapor pressure of pure 2-pentyne over the temperature range 25° to 75°. Agreement will be perfect at 25° and 56.12° with the maximum disagreement occurring at about 40° and 75°.

The varying amount of alkyne in the vapor phase was considered in the calculation of the cuprous chloride mole fraction for the solutions. The change in volume of the system due to the expansion of mercury and the liquid solution as a function of temperature was neglected. $(P_o - P)$ was of course corrected to pressure in terms of mm. of mercury at 0°.

Results. The results for the systems cuprous chloride 2-butyne and cuprous chloride 2-pentyne are summarized in Tables 32 and 33, respectively, as N/γ'. These values are plotted (with the anticipated error for the experiments when it is appreciable) as a function of temperature in Fig. 40. For both systems a general decline in N/γ' is indicated. The decline for the cuprous chloride 2-butyne system is well represented by a straight line. However, for the 2-pentyne system the rate of decrease, much greater at first, changes at about 44° to a lesser rate comparable with that of the cuprous chloride 2-butyne system. The variation of x_{CuCl} with temperature and its difference between the two systems is not expected to be of significance for the discussion.

At all times the solutions remained clear and colorless and at no time was a precipitate observed. Furthermore no reaction (as indicated by pressure measurements and appearance) took place even though the temperature of the system was about 50° for several days. Equal pressure changes, due to a possible reaction occurring to the same extent in both the solution and the pure solvent would of course go unnoticed.

Discussion of Results. The change of 11 percent in N/γ' for the cuprous chloride 2-butyne system over a 50° temperature range may not be of a significant nature due to the assumptions made at the end of the theoretical discussion. The author, however, believes that this change

Table 32

Δ P and N/γ' as a Function of Temperature for Cuprous Chloride Dissolved in 2-Butyne.

Ex.	No. of Obs.	T °C	Δ P mm.	P_o mm.	$\frac{\Delta P}{P_o}$x10^2	x_{CuCl}	$\frac{N}{\gamma'}$	
1	8	25.05	22.3	710	3.14	0.100	3.12	±0.05
2	2	29.41	28.6	826	3.46	0.100	2.89	0.03
3	8	30.26	27.6	851	3.24	0.100	3.09	0.03
4	4	37.64	36.3	1096	3.31	0.100	3.03	0.03
5	6	32.86	30.4	932	3.26	0.100	3.07	0.03
6	4	41.02	41.4	1225	3.38	0.101	2.98	0.02
7	2	41.87	42.6	1259	3.38	0.101	2.98	0.02
8	2	41.72	41.9	1253	3.34	0.101	3.01	0.02
9	8	51.80	59.4	1713	3.47	0.101	2.93	0.02
10	2	58.04	73.5	2054	3.58	0.102	2.84	0.02
11	4	58.16	73.4	2062	3.56	0.102	2.86	0.02
12	2	59.17	75.6	2122	3.56	0.102	2.86	0.02
13	4	75.16	123.7	3245	3.81	0.103	2.69	0.02
14	4	47.15	51.0	1488	3.43	0.101	2.95	0.02
15	4	67.18	96.7	2642	3.66	0.102	2.79	0.02
16	4	68.02	100.5	2701	3.72	0.102	2.75	0.02
17	8	43.57	45.1	1330	3.39	0.101	2.97	0.02
18	8	21.00	19.6	608	3.22	0.100	3.08	0.05
19	2	19.37	17.9	571	3.14	0.100	3.17	0.05

Table 33

P and N/γ' as a Function of Temperature for Cuprous Chloride Dissolved in 2-Pentyne.

1	4	25.05	5.4	238	2.27	0.106	4.66	±0.22
2	10	30.29	7.5	294	2.55	0.106	4.17	0.16
3	4	37.56	11.0	391	2.82	0.106	3.77	0.10
4	8	32.84	8.7	325	2.67	0.106	3.98	0.13
5	2	41.07	13.3	446	2.98	0.106	3.56	0.07
6	2	41.80	13.6	458	2.97	0.107	3.59	0.07
7	2	41.67	13.4	456	2.94	0.107	3.62	0.07
8	6	51.92	20.8	658	3.16	0.107	3.38	0.04
9	6	58.13	27.0	813	3.32	0.107	3.23	0.04
10	2	59.17	28.0	842	3.33	0.107	3.22	0.03
11	4	75.14	50.4	1394	3.62	0.108	2.98	0.03
12	4	47.25	17.3	558	3.10	0.107	3.44	0.06
13	2	68.02	38.3	1120	3.19	0.108	3.37	0.03
14	6	43.57	14.9	489	3.05	0.107	3.50	0.07
15	14	21.00	4.8	199	2.36	0.106	4.51	0.28
16	2	19.37	4.2	185	2.23	0.106	4.75	0.34

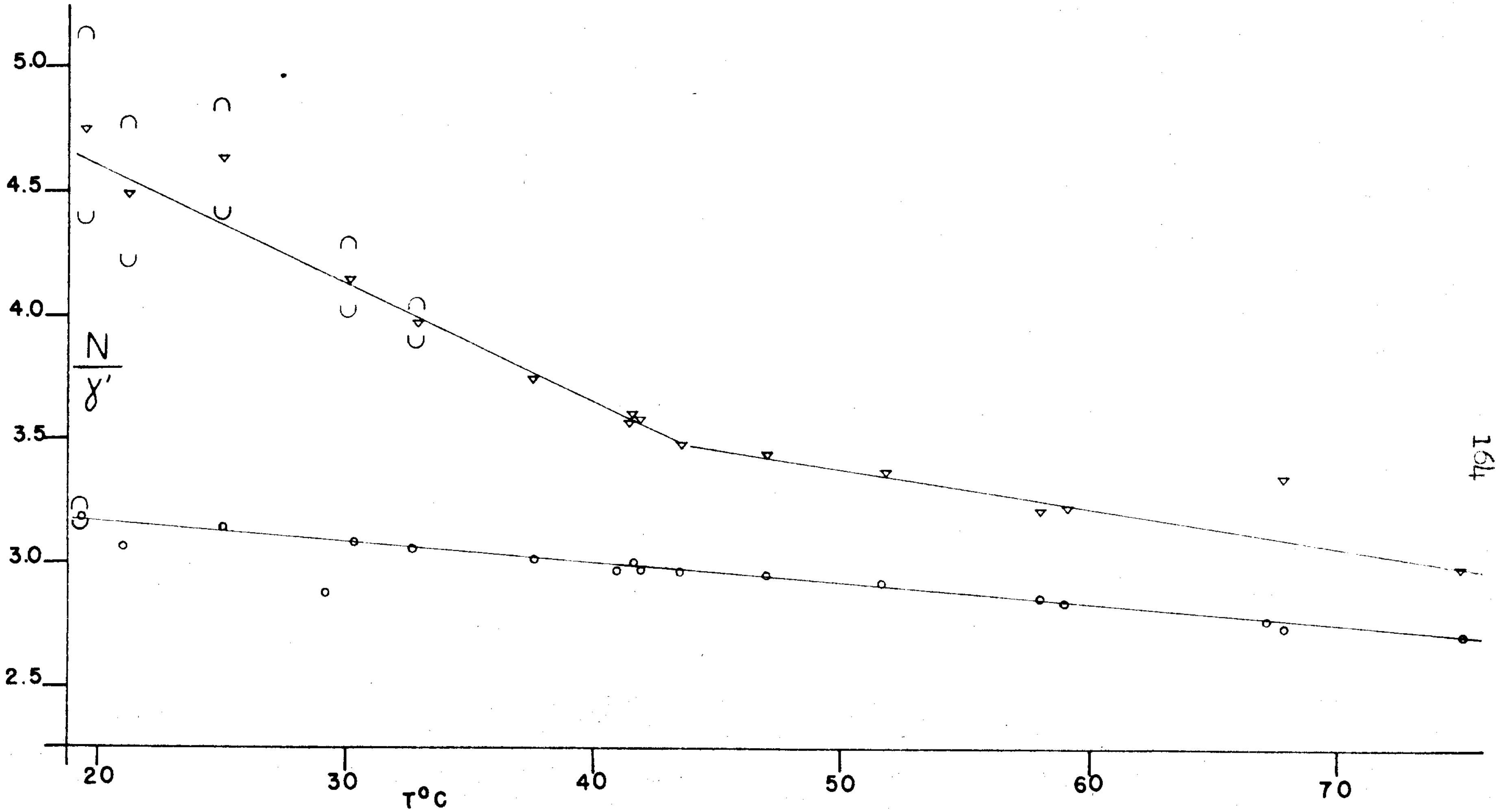


Fig. 40 N/ γ' as a function of temperature for 0.1 mole fraction cuprous chloride solution of 2-butyne and of 2-pentyne. Experimental value for; °, 2-butyne solution, ▿, 2-pentyne solution. The symbols ∩,∪ indicate the experimental error limit.

results from the variation of the chemical species present; expressively, that dissociation is occurring, the reaction for which has a low enthalpy change in the liquid phase. It appears in general that the total number of moles of solute slowly increases with temperature. The predominant species for the 2-butyne system appears to be the trimer. The same situation may be true for the cuprous bromide 2-butyne system at 25° at a much lower concentration since N/γ' was found to be 2.7 ±0.6 (Table 29).

Definite changes occur in the cuprous chloride 2-pentyne system in a 20° temperature range. N/γ' is reduced 25 percent, indicating that considerable dissociation takes place, possibly of the form eq. 58, with the breaking of cuprous

$$m(\mathrm{CuCl \cdot Un})_n\ (\mathrm{soln.}) = n(\mathrm{CuCl \cdot Un})_m(\mathrm{soln.}) \qquad (58)$$

halide bonds. However, at 45° the reaction appeared to be essentially complete. After 45° the 2-pentyne system was similar in its aspects (from Fig. 40) to what the 2-butyne system might be below 25°.

For both systems the continued decrease in N/γ' above 45° may be due to a reaction similar to eq. 59.

$$(\mathrm{CuCl \cdot Un})(\mathrm{soln.}) = \mathrm{CuCl}(\mathrm{soln.}) + \mathrm{Un}(\mathrm{soln.}) \qquad (59)$$

Experimental Details. The apparatus used for these experiments were constructed from two pyrex Erlenmeyer flasks

(10 ml.) joined to the opposite sides of a manometer constructed of 18-mm. tubing. Glass enclosed mites for magnetic stirring were placed in each flask. These were used in conjunction with the magnetic stirrer illustrated in Fig. 1. The tops of the flask were joined by tubing to form a "tee" and then to a standard taper ground glass joint. The joint, the length of straight tubing, and one of the flasks were coaxial. After the system had been degassed cuprous chloride was introduced into one of the Erlenmeyer flasks by a tared funnel through the above mentioned straight tubing. The apparatus was then evacuated and degassed for three days after which time the alkyne from storage prepared as indicated on pages 62 and 63 was condensed into both flasks and the tubing sealed. Approximately equal amounts of the alkyne were present in the two flasks after sealing. The weights of the materials used to form the solutions for the 2 systems were 0.604 g. of cuprous chloride, 3.357 g. of 2-butyne; and 0.607 g. of cuprous chloride, 3.592 g. of 2-pentyne. The volumes of the two systems at zero pressure difference at 25° were estimated as 26.2 ml. and 22.9 ml. for the cuprous chloride 2-butyne and cuprous chloride 2-pentyne systems respectively.

Inasmuch as the entire apparatus were submerged below the water level of bath No. 1, it was necessary to read the pressure differences through the glass walls of the jar. As previously checked with a graduated steel ruler in the bath no significant error (greater than ±0.15 mm.) was was introduced into the pressure measurements by the glass walls in the region of intended observation.

No observation was taken in less than 4 hours after equilibration at constant temperature. Intermittent stirring was provided during and after equilibration. Most observations were separated by at least 2 hours and in some cases up to 4 days. The average temperature deviation for Tables 32 and 33 is estimated at $\pm 0.03^{\circ}$. The thermometers used, graduated in hundreds of a degree, were calibrated at several temperatures with a certified N.B.S. thermometer. Stem corrections were applied.

N. INFRARED ABSORPTION BY THE CUPROUS HALIDE-ALKYNE COMPLEXES.

A survey of the infrared absorption spectra of the complexes of interest has been made. Solutions of cuprous chloride and cuprous bromide in pure alkynes (2-butyne, 2-pentyne, and 3-hexyne) are active in the infrared and show a sharp characteristic absorption peak at approximately 2080 wave numbers. For the 3-hexyne and 2-pentyne solutions this peak is a doublet with the less intense member at longer wavelengths. However, for the 2-butyne solutions the doublet is unresolved, and the characteristic peak has a shoulder also at longer wavelengths.

Experimental Details. The instrument employed in this study was a double beam, automatic recording, Perkin-Elmer infrared spectrophotometer. The spectra of the solutions were recorded in a 1.0-mm. sodium chloride cell with the pure hydrocarbon in the matching cell. Solutions of known concentrations were prepared in the apparatus shown in Fig. 41. The cuprous halide was introduced into the apparatus by means of a funnel through stem "S". The apparatus was then reweighed, fitted with a new size A serum bottle stopper, and evacuated. A known weight of alkyne was distilled into the flask and the cuprous halide dissolved. Prior to the removal of solution nitrogen at one atmosphere was admitted to the apparatus. The solution was removed from the apparatus in the absence of air and transferred to the cell with the aid of a hypodermic syringe.

Nitrogen pressure in the apparatus aided the removal of the 2-butyne solutions. The stopcock of the apparatus was greased with "Silicone".

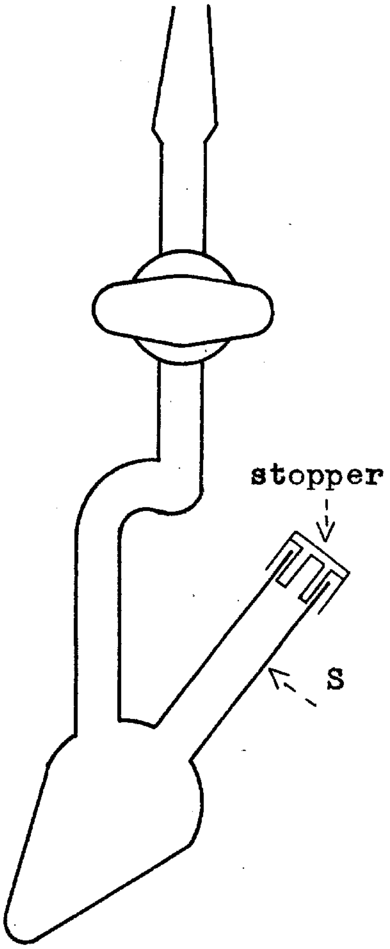


Fig. 41 Apparatus for the preparation of solutions.

Results. The results of the survey are indicated in Table 34. The second column in the table indicates the member of the doublet described for those absorption peaks which are split; 1 denotes the member of the doublet at the higher frequency. In the succeeding columns are given the carbon-carbon triple-bond stretching frequencies for the various alkynes and the separation $\Delta 1/\lambda^*$ of their doublets; the position of the absorption peaks $1/\lambda$ for the solutions and the separations $\Delta 1/\lambda$ of their doublets; the approximate extinction coefficients, E, calculated according to eq. 60, where ℓ is the length of the path; the mole fraction of cuprous halide in solution; and the frequency difference, $(1/\lambda^* - 1/\lambda_{\text{max.}})$ where λ^* refers to the wavelength in centimeters

Table 34

The Observed Frequency Shift of the Maximum of the Triple-Bond Stretching Mode for Complexed Alkynes.

System	Doublet	Absorption Peak and Separation of Doublets.				E^b	x_{CuX}	Shift $\left(1/\lambda^* - 1/\lambda_{max}\right)$	
		Pure Alkyne[a]		Solution					
		$1/\lambda^*$	$\Delta 1/\lambda^*$	$1/\lambda$	$\Delta 1/\lambda$				
		cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$		cm.$^{-1}$	%
CuCl 2-Butyne	1	2310	77	2095	35	120	0.0475	176	7.75
	2	2233		2060[c]		55			
CuBr 2-Butyne	1	2310	77	2101		130	0.0139[d]	170	7.50
	2	2233				38			
CuCl 2-Pentyne	1	2304	66	2094	31	110	0.0497	177	7.80
	2	2238		2063		53			
CuBr 2-Pentyne	1	2304	66	2103	32	85	0.0472	168	7.40
	2	2238		2071		30			
CuCl 3-Hexyne	1	2301	70	2087	50	120	0.0485	177	7.82
	2	2231		2037		24[e]			
CuBr 3-Hexyne	1	2301	70	2083	55	100	0.0483	183	8.10
	2	2231		2028		16			

[a] Raman spectra data; summarized (49).

[b] for comparison, E = 230 cm.$^{-1}$ for the carbon-hydrogen stretching frequency (3.415 microns) of 3-hexyne.

[c] shoulder only.

[d] the cuprous bromide-2-butyne complex has low solubility in the pure alkyne.

[e] for x_{CuCl} = 0.1188, E = 24 cm.$^{-1}$ also.

of the carbon-carbon triple-bond stretching frequency and where $\lambda_{max.}$ refers to the wavelength of the strongest

$$\text{Optical Density} = E \, \ell \, x_{CuX} \qquad (60)$$

maximum of the absorption peak of the cuprous-halide alkyne solutions.

The exact positions of the absorption peaks for the solutions are in some doubt as they occur in places where the alkyne is moderately strongly absorbing and where the optical density of the alkyne is rapidly changing. The maximum error for the positions of the maxima as listed in Table 34 is estimated as ± 5 cm.$^{-1}$.

For the pure cuprous chloride and cuprous bromide solutions the strongest absorption peaks observed in the range 2-15 microns are those characteristic ones at 2080 cm.$^{-1}$. Other absorption peaks observed are very broad in comparison and occur at longer wavelengths. Some of the peaks are probably spurious as they occur in regions where the solvent is very absorbent, and the intensity of other peaks seems to depend strongly on the purity of the cuprous halide. However evidence for this latter observation is scant. The low solubility of the cuprous bromide-2-butyne complex severely restricts the range of concentrations which can be studied.for the cuprous bromide 2-butyne system.

Discussion. It is unlikely that the presence of the absorption peaks of cuprous halide solutions can be correctly attributed to the vibration spectrumof the cuprous halide molecule. A large change in frequency would be expected when cuprous bromide is substituted for the cuprous chloride in solution. This was not observed.

The activity of the solution in the infrared at 2080 $cm.^{-1}$ is very likely due to the carbon-carbon triple-bond stretching mode activated by the presence of the copper atoms. The electronic structure of the triple-bond in the complex has apparently undergone a profound change but in the concepts of current usage, the triple-bond is still present. The triple-bond stretching frequency ($1/\lambda^{*}$) for the alkyne in Table 34 is not infrared active in the presence of ordinary solvents. Its activity associated with the presence of cuprous halide indicates that a dipole moment, which changes as the carbon atoms move in the directions of the normal vibrations for the frequency considered, is present in the complexes. The constancy of the supposed shift (<u>ca</u>. 175 wave numbers) independent of the system is strong evidence for the above explanation.

The magnitude of the shift is a measure of the influence of the copper atom. Taufen, Murray, and Cleveland, (50), observed in Raman spectra a frequency shift of 60-70 $cm.^{-1}$ for the carbon double-bond stretching mode of four olefins dissolved in concentrated aqueous silver salt solutions. For mono-alkyl or-aryl substituted acetylenes in concentrated aqueous silver salt solutions they observed a frequency shift of approximately 118 $cm.^{-1}$ in the triple-bond stretching mode. However, they indicated that the alkyne was probably in solution as the acetylide. Chatt (51), for a number of the platinous chloride-olefin complexes, reported a frequency shift of approximately a 143 wave numbers. In magnitude then the largest shift observed for metal salt-unsaturated hydrocarbon complexes has been in the cuprous halide-alkyne series. Percentagewise (i.e., $(1/\lambda^{*}-1/\lambda_{max.})/\lambda^{*} \times 100$) the shift for the cuprous halide alkyne systems is almost as large as that (8.70 percent) observed by Chatt for the very stable (in comparison) platinous chloride-olefin complexes.

Doublets. The doublet observed in Raman spectra at approximately 2270 $cm.^{-1}$ for pure alkynes containing the carbon skeleton $C - C \equiv C - C$ has been a subject of some interest inasmuch as it was unexpected. The most probable explanation (49) was first offered by Badger (52). His suggestion was that the doublet was an example of Fermi resonance (53), i.e., accidental degeneracy, caused by the frequency coincidence of an overtone of a carbon-carbon single-bond stretching mode with the triple-bond stretching mode. It should be remarked that the maxima of the doublet have equal intensities. As indicated in Table 34 the separation of the maxima is approximately 72 wave numbers.

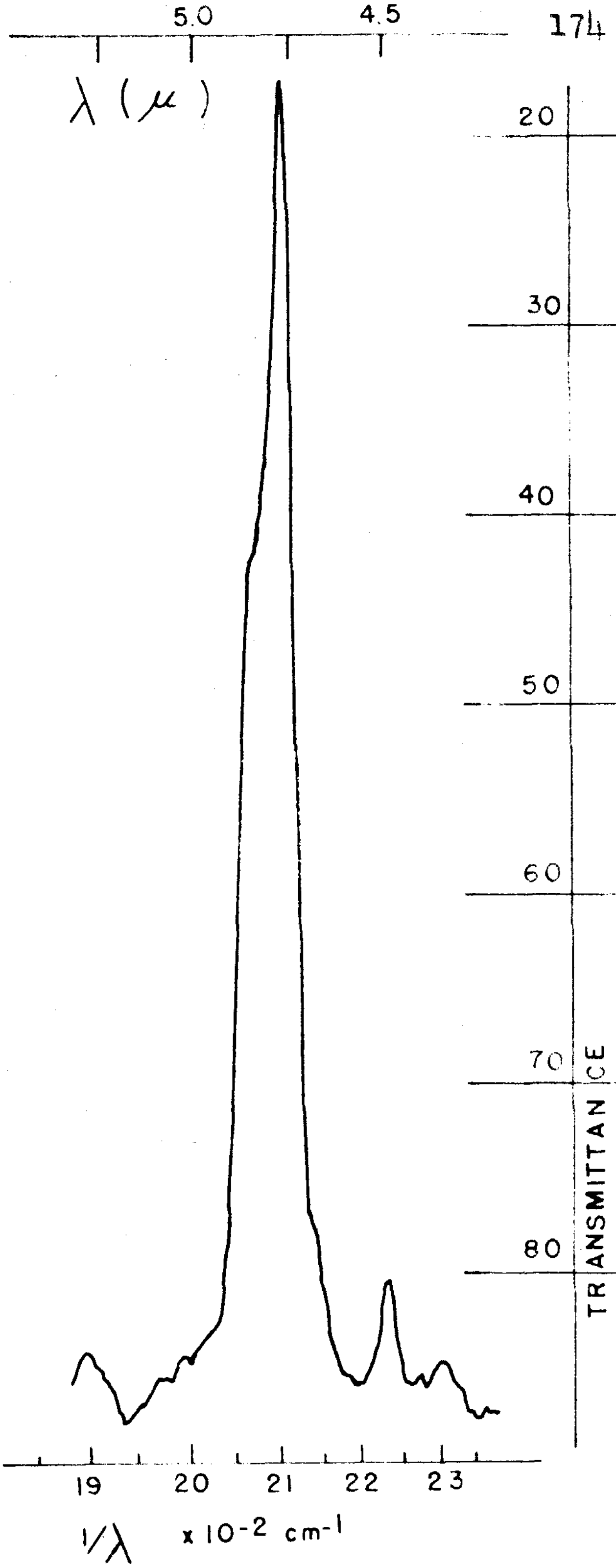


Fig. 42 Infrared absorption spectra for 2-butyne solution containing cuprous chloride (4.75 mole percent).

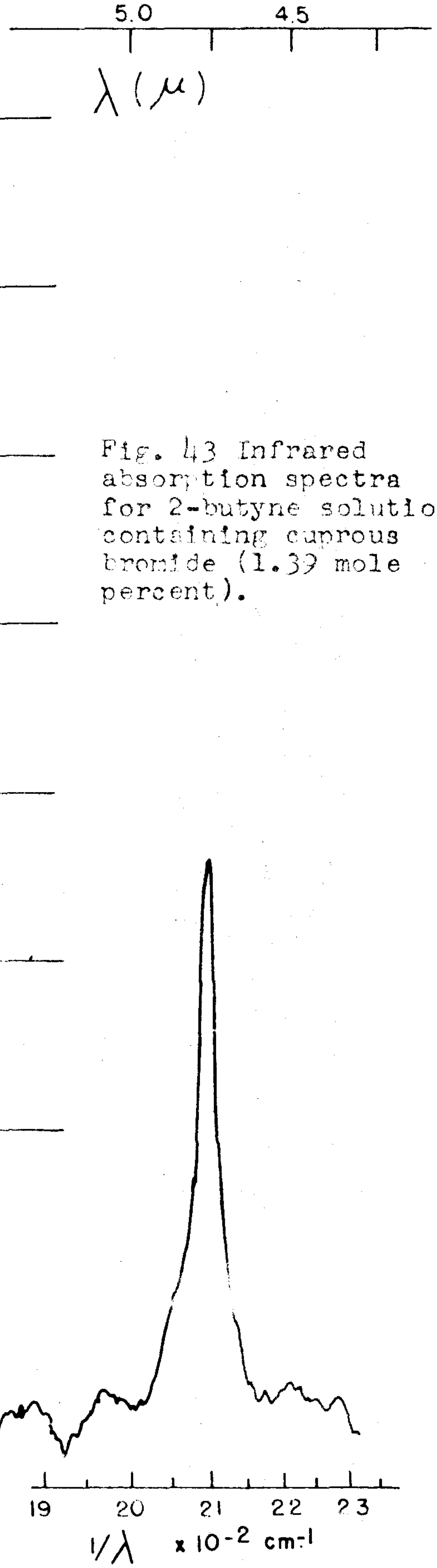


Fig. 43 Infrared absorption spectra for 2-butyne solution containing cuprous bromide (1.39 mole percent).

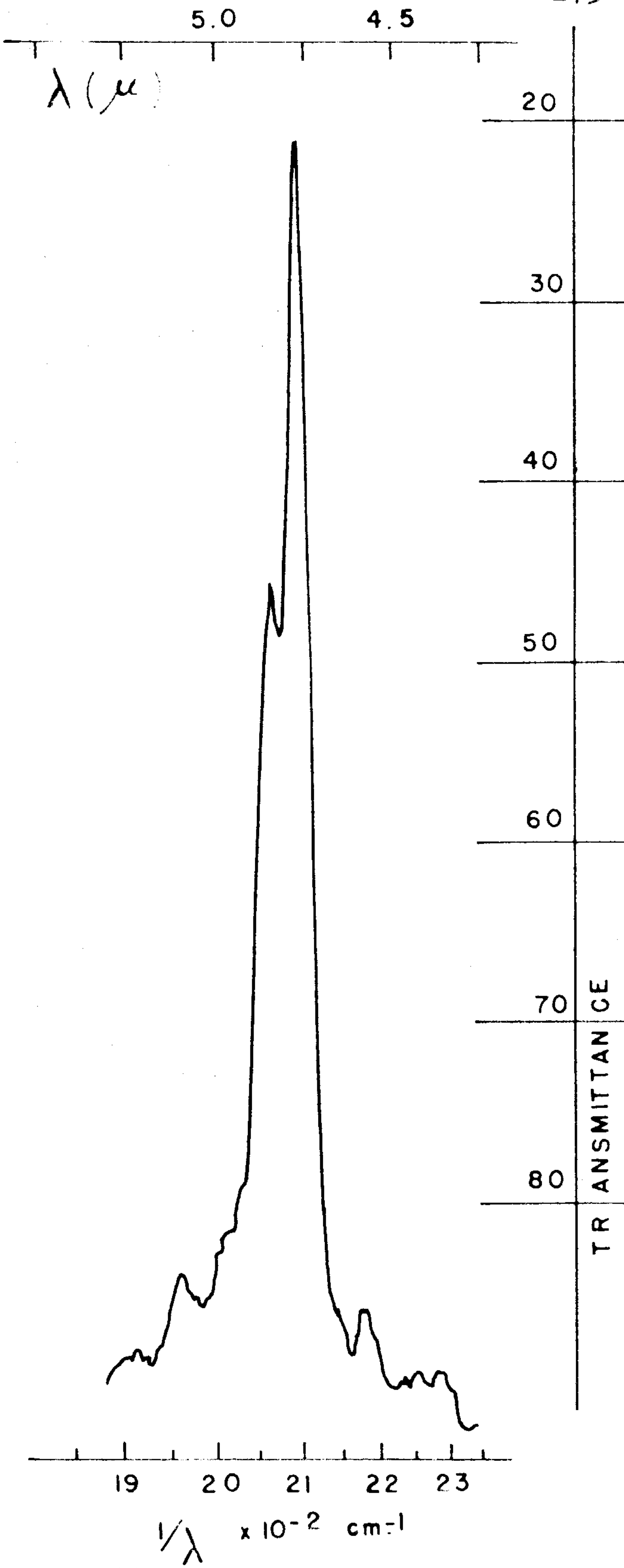


Fig. 44 Infrared absorption spectra for 2-pentyne solution containing cuprous chloride (4.97 mole percent).

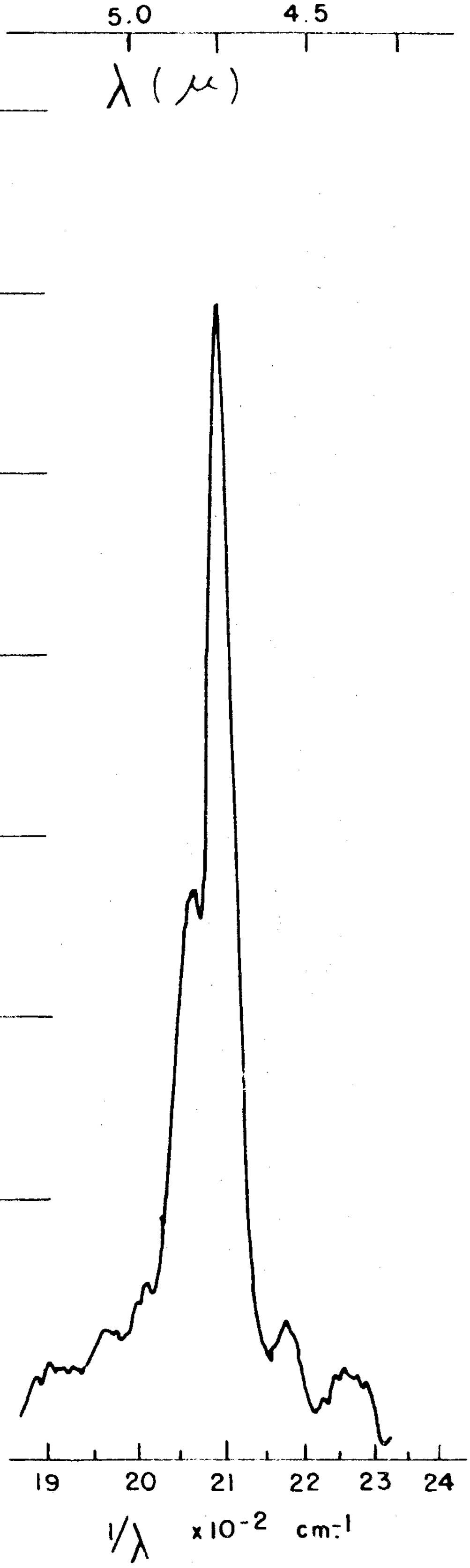


Fig. 45 Infrared absorption spectra for 2-pentyne solution containing cuprous bromide (4.72 mole percent).

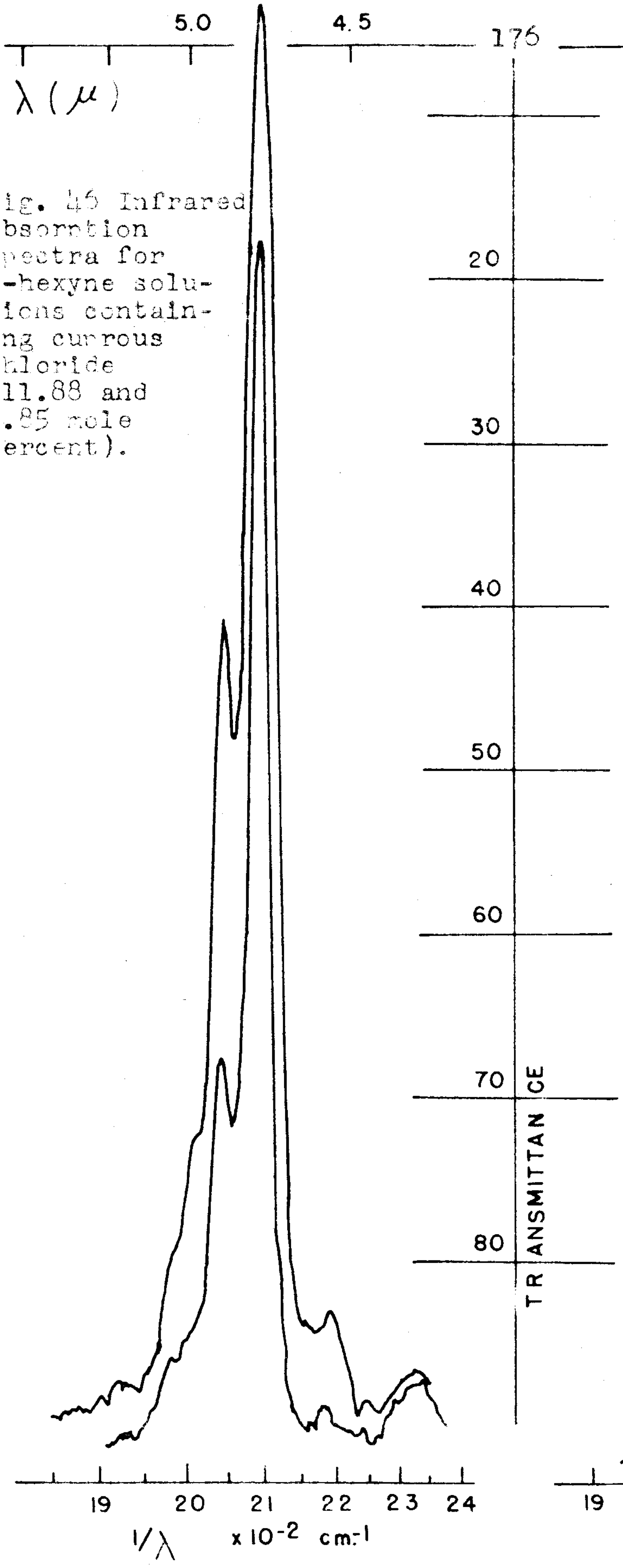


Fig. 46 Infrared absorption spectra for 3-hexyne solutions containing cuprous chloride (11.88 and 4.85 mole percent).

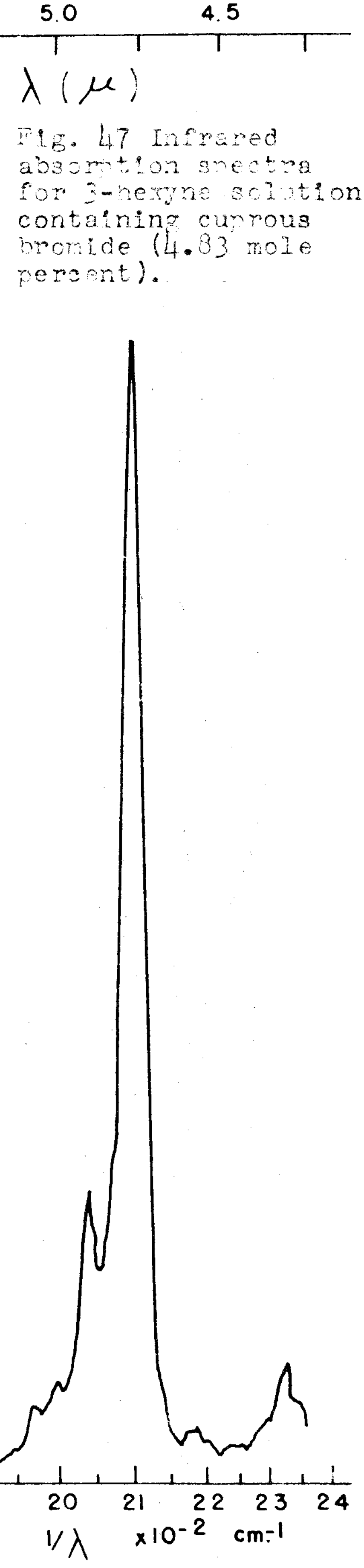


Fig. 47 Infrared absorption spectra for 3-hexyne solution containing cuprous bromide (4.83 mole percent).

The doublets observed (2-pentyne and 3-hexyne solutions) in this study are illustrated in Fig. 42 to 47. It is seen at once that the maxima are not of equal intensity and that little or no absorption is present in the 2270 $cm.^{-1}$ region. The suggestion* that these doublets may be examples of Fermi resonance (less pronounced) is supported by the observation that the frequency shift is constant for each alkyne. The mode of vibration whose overtone is responsible for the degeneracy is uncertain and plausible guesses as to its identity must await definite structural information. If the carbon-carbon stretching mode mentioned above in connection with the pure alkyne Fermi resonance is also related to the doublets observed in the spectra of the cuprous halide alkyne solutions, then the force constant for this carbon-carbon stretching mode must be lowered an amount proportional to the percentage decrease observed for the triple-bond of those alkyne molecules which are complexed*. Hence, this hypothesis would require that both the carbon-carbon triple bond and the adjacent single bonds would change their bond lengths (increase) and bond order (decrease). In a similar case the stretching frequencies of the carbon-hydrogen bond adjacent to the double-bond in olefins has indeed been observed to shift to longer wavelengths when the olefins were complexed in aqueous silver nitrate solutions (50).

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*Professor Badger, private discussion.

However, other explanations are by no means excluded. The possibility of several complex species in solution has already been mentioned. Thus it may be that the triple-bond stretching frequencies for the different species are separable into two main groups. One possible species which would account for an additional lowering of the triple-bond stretching frequency is that characterized by the interactions of a single alkyne molecule with two cuprous halide molecules. However, this possibility is not supported by the meager evidence available. The extinction coefficient E for the less intense maxima as calculated by eq. 60 does not show a dependency in the expected manner upon total cuprous halide present.

O. ULTRAVIOLET ABSORPTION BY THE CUPROUS HALIDE-ALKYNE COMPLEXES IN n-HEPTANE.

In view of the necessary electrodynamic nature of complex bond formation it is reasonable to expect that changes in the ultraviolet spectra of olefins and alkynes will accompany their molecular association with metal salts. These expected changes have not been noted* for the cuprous chloride-olefin complexes** (54), possibly because the investigators did not examine the spectra below 3200 A.

However, cuprous chloride and cuprous bromide dissolved in heptane solutions of disubstituted alkynes absorbed strongly in the ultraviolet (2200 - 2700 A).

Experimental Details. n-Heptane solutions containing 1 to 6.6 mole percent alkyne were prepared with the aid of the high vacuum apparatus. Known weights of cuprous chloride and cuprous bromide were dissolved in weighed amounts of heptane-alkyne solutions in glass stoppered flasks. Fused silica cells with a path length of 1 cm. were used: the compensating cell was filled with the heptane-alkyne solutions. This work was expedited by the availability of

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* To the author's knowledge the ultraviolet spectra of the platinous chloride-olefin complexes have not been investigated, although these complexes are yellow.

** The strongly colored (yellow) cuprous chloride complexes of dicarboxylic acids, such as fumaric and maleic acids, obviously represent special cases (55, 54).

a "Cary" Recording Spectrophotometer in the Crellin laboratories.

Commercial n-heptane was purified as described by Helmkamp (56).

Results. Table 35 gives the concentration of the alkyne in mole percent; the concentration of cuprous halide in mole percent and in moles per liter of solution; $\lambda_{max.}$, the wavelength of the maximum of the absorption peaks; and $E_{max.}$, the molar extinction coefficient for $\lambda_{max.}$. The spectra as a function of cuprous halide concentration for the systems, heptane 2-pentyne cuprous bromide and heptane 3-hexyne cuprous chloride are indicated in Fig. 48 and 49. The variation of $\lambda_{max.}$ and $E_{max.}$ for the latter system as a function of cuprous chloride concentration is shown in Fig. 50 and 51 respectively. In general the observed absorption in the ultraviolet is between the wavelengths 2200 A and 2700 A. However, heptane-3-hexyne solutions containing large amounts of cuprous chloride absorb strongly as far as 3100 A. At this wavelength the absorption spectrum declines very rapidly to a negligible optical density: no absorption is noticeable at greater wavelengths.

Discussion. As in the case of the infrared spectra the general shape and position of the absorption curves in the ultraviolet are not dependent on the halide but dependent only on the alkyne. Thus Fig. 48 is characteristic for the heptane solutions containing 2-butyne and

Table 35

Ultraviolet Spectra of Molecular Complexes in Heptane; $\lambda_{max.}$ and Molar Extinction Coefficient as a Function of Concentration.

Alkyne	Cuprous Halide	Concentration			$\lambda_{max.}$		$E^{a}_{max.}$
		Alkyne mole%	Cuprous Halide[a] mole% x 10^2	molar[b] x 10^3	A		$(M.cm.)^{-1}$
2-Butyne	CuCl	6.18	0.781	0.544	2349	3	4500
	CuBr	6.18	0.584	0.407	2337	5	5250
2-Pentyne	CuCl	6.61	0.571	0.397	2278		7410
	CuBr	6.61	0.433	0.300	2275	3	8350
		6.61	0.374	0.259	2259	5	7480
3-Hexyne	CuCl	4.71	0.814	0.557	2323		4760
		1.10	1.393	0.947	2403		3180
		1.10	0.900	0.612	2360		4030
		1.10	0.669	0.458	2340	7	4820
		1.10	0.400	0.272	2300	3	6340
		1.10	0.199	0.135	2275		8160
	CuBr	4.71	1.370	0.938	2398	5	3350
		4.71	0.556	0.381	2289		5660

a Error about 1-1.5 percent, based on x_{CuX} (total).
b Calculated on the basis of known densities at 25°; the temperature however was not controlled.

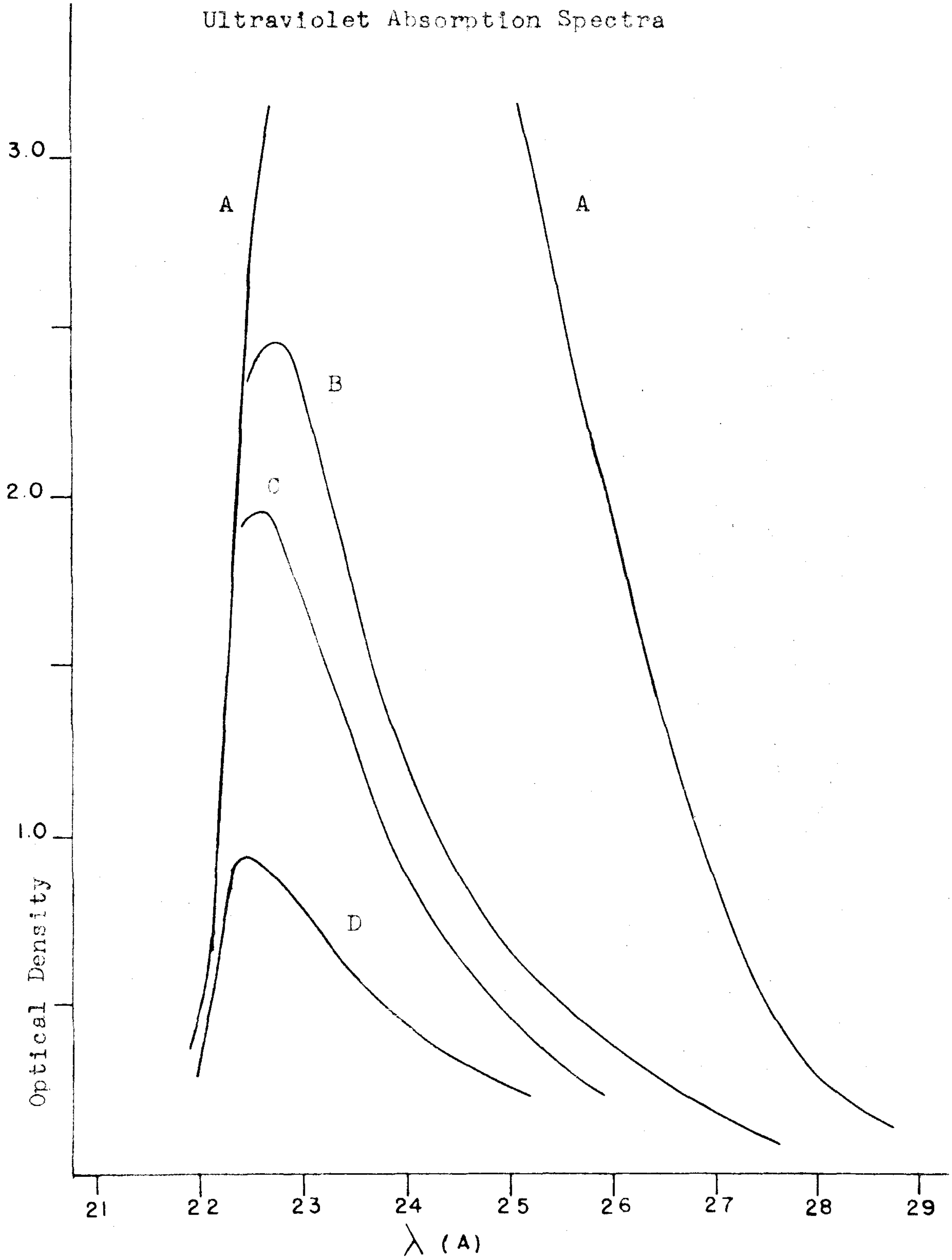

Fig.48 Ultraviolet absorption spectra for n-heptane solutions containing 2-pentyne (6.61 mole percent) and cuprous bromide (A, 0.00152 M; B, 0.00030 M; C, 0.00026 M; D, unknown concentration).

Ultraviolet Absorption Spectra

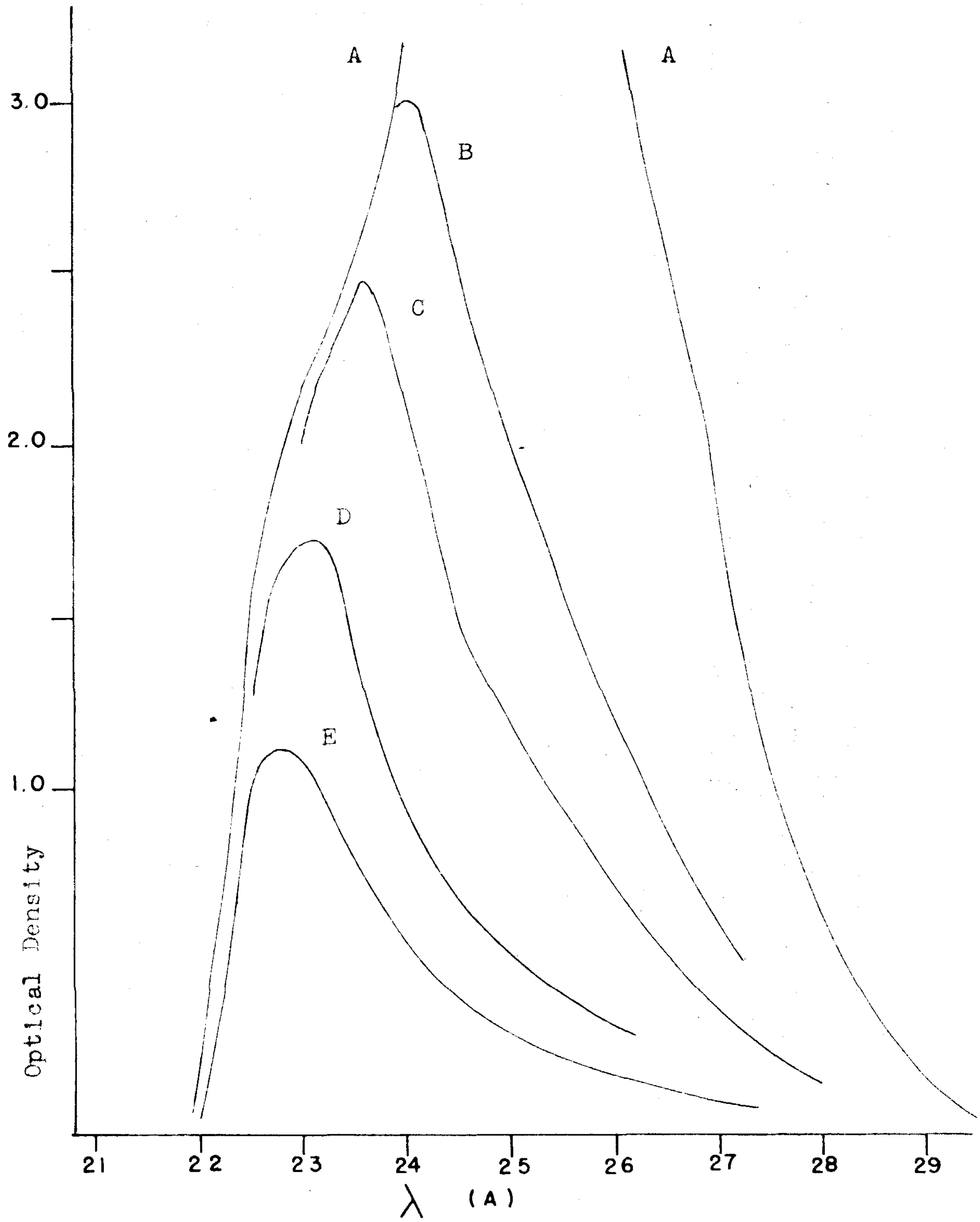

Fig. 49 Ultraviolet absorption spectra for n-heptane solutions containing 3-hexyne (1.10 mole percent) and cuprous chloride (A, 0.00292 M; B, 0.00095 M; C, 0.00061 M; D, 0.00046 M; E, 0.00027 M).

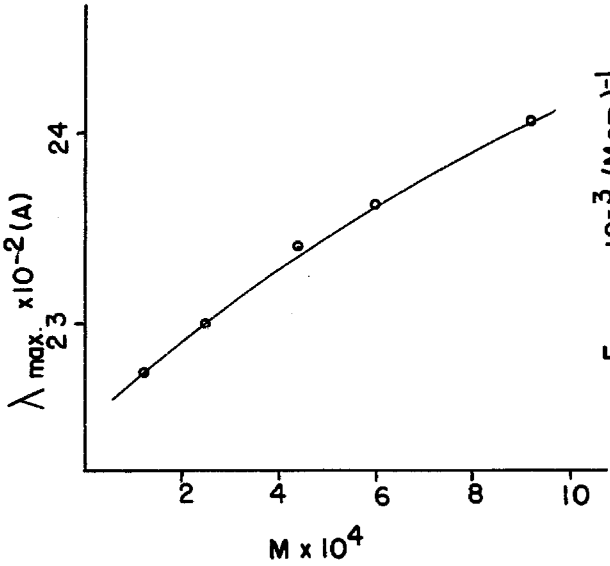

Fig. 50 $\lambda_{max.}$ as a function of cuprous chloride concentration in 3-hexyne (1.1 mole percent)-heptane solution.

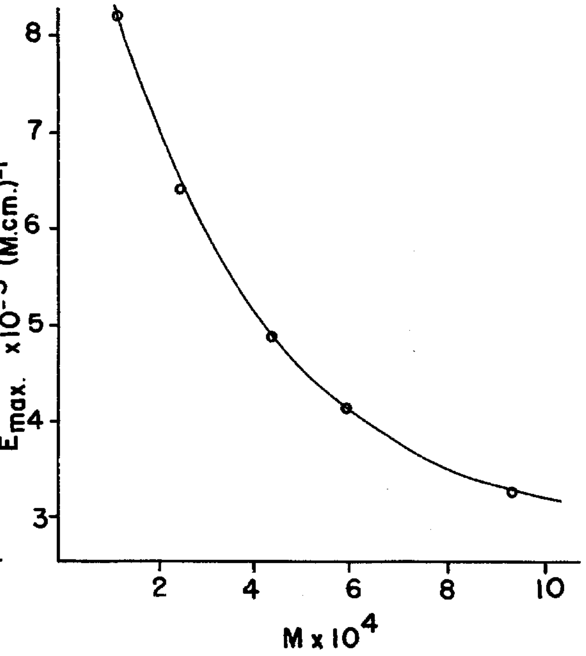

Fig. 51 $E_{max.}$ as a function of cuprous chloride concentration in 3-hexyne (1.1 mole percent)-heptane solution.

cuprous chloride or cuprous bromide, and 2-pentyne and cuprous chloride or cuprous bromide, and Fig. 49 is characteristic for the heptane solutions containing 3-hexyne and cuprous chloride or cuprous bromide. Detailed features such as the exact values of $\lambda_{max.}$ and $E_{max.}$, however depend on the cuprous halide concentration and on the alkyne concentration. Hence, it is immediately apparent that more than one species in solution is responsible for the absorption spectra. Fig. 51 shows graphically that the species primarily responsible for the spectra at shorter wavelengths in the alkyne cuprous chloride solution are more strongly absorbent than those that absorb at higher wavelengths. However, Fig. 49 indicates that their concentration remains almost independent of the total cuprous chloride present after x_{CuCl} reaches a certain value. Hence, there is little doubt that in these solutions an equilibrium is involved between two or more species.

Although the identities of the different species are unknown their intense absorption is certainly due to the presence of the cuprous halide since acetylene and alkynes absorb only weakly in the wavelength range 2200-2700 A (57).

P. THE UNIT CELL AND SPACE GROUP OF CUPROUS CHLORIDE-2-BUTYNE COMPLEX.

Introduction. In view of the paucity of our knowledge concerning the configuration of the components in the cuprous halide-alkyne complexes, it was considered desirable to undertake a structural analysis of a representative member stable at room temperature. Due to the non-volatility of the complex as such, electron diffraction methods are inapplicable. Since single crystals of the complexes were available an x-ray investigation was initiated. The cuprous chloride-2-butyne complex was chosen because of the expected simplicity of the organic component and the favorable atomic numbers of the inorganic component.

Unit Cell and Space Group. The dimensions of the unit cell and the possible space group of the crystalline complex cuprous chloride-2-butyne, were determined from the diffraction patterns of single crystals sealed in thin-walled capillaries. The complex was found to be monoclinic with the following dimensions:

$a = 10.36 \pm 0.01$ A $c = 13.00 \pm 0.01$ A
$b = 8.80 \pm 0.01$ A $\beta = 96.62 \pm 0.10^\circ$

On Weisenberg photographs of the (h0l) layer made with unfiltered copper K_α radiation and with copper K_α radiation filtered through nickel, reflections from the respective planes were observed up to $h = 13$ and $l = 16$. The intensities measured from multiple photographs varied from 1 to 3300 on an arbitrary scale. Of the approximate 720 possible reflections in the (h0l) layer 134 were actually observed. All of these were of the form $h + l = 2p$, where $p =$ an integer. Equi-inclination Weisenberg photographs of the next seven layers were taken using copper radiation.

The (0k0) reflections were examined up to $k = 13$ using the procession camera with molybdenum K radiation and a zirconium filter. In particular the (0kl) net was observed. Of the (0k0) reflections roughly 50 percent of the total observed intensity was associated with the odd reflections. Hence, a twofold screw axis is not expected to be present. Similarly, reflections of all other types were present. The probable space groups are $C_s^2 - Pn$ and $C_{2h}^4 - P\frac{2}{n}$.

The temperature of the crystal during the determinations of the lattice constants was taken to be that of a thermometer lying on the base of the camera, _i.e._ 27.0 ± 0.5°. The density of the crystal at this temperature was calculated to be 1.727 ± 0.006 g./ml. assuming 8 molecules of the form $CuCl \cdot C_4H_6$ per unit cell and assuming the formula of the density (57) to be eq. 61. The density as measured at 25.00° (see Table 27) was 1.730 ± 0.003 g./cm..

$$d_c = \frac{1.6602}{abc \sin \beta} \sum_{\substack{i \\ \text{unit cell}}} \text{atomic wt. of atom } i \qquad (61)$$

Details of Investigation. The single crystals used for the x-ray analysis were prepared as follows: approximately 0.2 g. of cuprous chloride was introduced in an apparatus similar to Fig. 2 by means of a long stemmed funnel. The apparatus was then evacuated and by high vacuum technique approximately 1 ml. of 2-butyne was condensed into bulb "B". The apparatus was then sealed and the ground glass joint removed. When the seal was cool the apparatus was inverted and the cuprous chloride allowed to react with the 2-butyne. The solution was then allowed to enter the capillary. Crystals were formed as the excess butyne was carefully distilled into bulb "B" which for this purpose was placed in a bath the temperature of which was somewhat below ambient. Examination of the crystals thus formed with a polarizing microscope indicated their desirability. Undesirable crystals were dissolved in the alkyne by the local application of heat, i.e. the approach of a hot wire. Repetition of this gave single crystals which filled the entire capillary and whose b axis was parallel, within 2°, to the axis of the capillary. The length of these crystals was increased by placing the entire apparatus in a bath that was slowly warmed to approximately 35° and allowed to cool over night to 0°. This method was repeated until the length of the single crystal which filled the capillary was approximately 4 mm. long. The apparatus for growing the crystals was prepared as below. An x-ray capillary

(0.23 mm.dia) was joined to pyrex via a graded seal between pyrex and lead glass. The apparatus before use was thoroughly washed with distilled water and redistilled acetone. Considerable care was used in the construction and handling of the apparatus as the x-ray capillaries were fragile.

The single crystals were sealed in the respective capillaries by means of a tiny gas-oxygen flame. For proper sealine and to protect the desired crystal from the solvent effect of hot excess alkyne it was necessary to remove excess solution and unwanted crystals from the immediate locality of the seal. However, it is thought advantageous to seal a small excess of solution with the single crystal as this practice seems to delay the destruction of the crystal by radiation. Sealing wax was used to coat the glass seal. However, in two attempts where a microscopic examination of the sealing wax revealed no imperfection in the coating the single crystal was destroyed within 24 hours through the loss of 2-butyne.

Prolonged exposure of the single crystal to x-ray radiation (either copper K_α or molybdenum K_α) resulted in its ultimate destruction. In the cases of well sealed samples (as indicated by the long life of the crystalline complex) the path toward destruction was as follows:

(i) After approximately 50 hours of exposure (for copper K_α, 15 ma. at 40 K.V.) the irradiated portion of the sample developed a light yellow color that did not appreciably increase in intensity with the increased exposure. Low order diffuse spots were apparent on heavily exposed film. About half of these spots seemed unrelated to any expected reflection.

(ii) By comparison with the appearance of the unexposed sample, the exposed sample showed an increased volume after 100 hours of exposure. This was surmised from the greater reflecting power of the irradiated portion; it appeared that it was in closer contact with the capillary wall than the remaining part of the crystal.

(iii) After 200 hours exposure the relative intensity of the diffuse spots had considerably increased (factor of about 50 percent). Multiple fractures appeared throughout the exposed portion of the crystal but not in the adjoining unexposed crystal. Shortly after this event the diffraction photographs indicated the presence of randomly oriented cuprous chloride crystals and the exposed portion of the crystal became somewhat opaque. This catastrophe did not spread to the unexposed crystal, but was limited rather sharply to the radiated volume.

Since the unique crystal axis was in the direction of the cylinder axis the polarizing microscope and the Laue diffraction camera were useful in orienting the crystals.

The length of the l axis was determined using nickel filtered copper K_α radiation from two oscillation photographs, (15° oscillations) which were calibrated with fiducial marks. The diameter of the camera used was 10.016 ±0.002 cm..

The axial lengths a and c, and the angle β were determined with the aid of a single crystal rotation photograph using copper K radiation filtered through nickel. The camera diameter was approximately 10 cm. and the film arrangement used was that of Straumannis. The back reflections observed on the photograph were indexed with the assistance of a zero layer Weisenberg. These reflections and their intensities on the scale mentioned above were ($\overline{10}$ 0 6), (5 0 11), (4 0 12), (0 0 14), ($\overline{10}$ 0 8), and 46, 43, 17, 15, 25 respectively. On the rotation photographs the reflections ($\overline{10}$ 0 6) and (5 0 11) were superimposed upon one another. The calculated separation of the reflections due to the wave length difference of $K_{\alpha 1}$, and $K_{\alpha 2}$ was equal to the observed separation within experimental error. The observation of the superimposed reflections was not confused by the presence of any other reflection of appreciable magnitude. The width of the reflection was found to be the same as that of ($\overline{10}$ 0 8) and (4 0 12) within experimental error.

In the calculation of a and c the cosβ term was eliminated from the equation for $1/d_{(\overline{10}\ 0\ 6)}$ and $1/d_{(5\ 0\ 11)}$. This was tantamont to taking a weighted average in $1/d_{hkl}$ measure; the respective weights were 11 and 12. Since the reflections were superimposed or very nearly so and since their relative intensities were the same within experimental error the measurements of the scattering angle on the rotation photograph of the combined reflections was the same as taking a weighted average position in 'scattering angle measure' where each spot was weighted equally. Thus the procedure of eliminating the cosine term results accidentally in an equation which was relatively insensitive to the actual location of the reflections as long as the average position of the two spots was nearly correct. This led to an equation which had less error associated with it than would be the case if the two reflections were distinct and hence measured separately.

Following Bragg (57) it was assumed $\lambda_{K_{\alpha_1}}$ equals 1.5405 A° and $\lambda_{K_{\alpha_2}}$ equals 1.5443 A°. The measured scattering angle was corrected for the shift due to the absorption of radiation by the sample assuming a divergent beam and assuming that the mass absorption coefficient equals 0.1 (calculated; 0.103) (58).

Q. OTHER SYSTEMS STUDIED.

The investigation of the reaction of the triple bond with cuprous and silver salts was extended to other systems in order to note the universality of the reaction and the general characteristics which might be associated with the complexes formed. The ligands studied include not only other alkynes and alkyne derivatives but also acetonitrile. This latter ligand was chosen because of the relationship of its functional group to the carbon-carbon triple bond and because of its volatility (100 mm. at 27°), which is comparable to that of 3-hexyne.

Some of the preliminary studies described below were carried out in stoppered test tubes, others were made under oxygen-free conditions in ampoules (see page 24).

System; Cuprous Chloride and 2-Heptyne. Although 2-heptyne dissolves considerable qualities of cuprous chloride to form a colorless viscous liquid no crystalline products have been observed. The ampoule containing the system has been studied under a variety of conditions and has been at ambient temperatures for 9 months. The liquid decomposes under low heptyne pressure to the starting materials.

The 2-heptyne had been previously prepared by Helmkamp (59) and stored in oxygen-free ampoules.

System; Cuprous Chloride and 2,2,5-Trimethyl-3-hexyne. This alkyne readily reacts with cuprous chloride in an ampoule to give small, clear, colorless crystals. The alkyne was obtained from an ampoule prepared by Helmkamp (60).

System; Cuprous Chloride and Di-t-butylacetylene. In a sealed ampoule cuprous chloride dissolved in the branched alkyne to form a colorless crystalline solid when chilled briefly at 0°. This solid is stable at room temperature and is not easily decomposed compared to the 3-hexyne complexes. The decomposition point however is not known. The crystals are small laminae similar to that indicated in Fig. 16.

The alkyne had been prepared by Helmkamp (61) and had been stored in a sealed ampoule free of oxygen.

System; Cuprous Chloride and 2-Heptyne-1-ol. The complexes formed by this system can be prepared by mixing sufficient cuprous chloride with the organic phase. When this is done a very viscous solution is obtained which soon solidifies to form very small colorless needles. At about 40° these needles are quite soluble in excess alkynol. On a hot stage melting point apparatus the crystals melt at 46.8° and the melt decomposes at 49° into cuprous chloride and the liquid alkynol.

2-Heptyn-1-ol was used as received from Farchan.

System; Cuprous Chloride and 3-Heptyn-1-ol. The complex crystals of this system are quite different in some characteristics from those described above. Although cuprous chloride is quite soluble in the alkynol the complex crystals are not readily formed. They appear after a week's time at room temperature. The solution was protected during this time since oxidation of the copper halide had been noticed after 2 days in an unstoppered tube. Once formed, the colorless crystals are very hard and decompose on a hot stage melting point apparatus at 153-156°. 3-Heptyn-1-ol was used as received from Farchan.

<u>System; Cuprous Chloride and 2,5-Dimethyl-3-hexyne-2,5-diol</u>. Warm concentrated acetone solutions of the alkyndiol dissolve small amounts of cuprous chloride to form colorless crystals when the solutions are cooled to about 15°. The reaction product is stable for long periods of time in the presence of air. However, slow oxidation of the cuprous chloride gives the product a light green appearance after the passage of a year.

When examined on a hot-stage melting point apparatus the complex crystals are first observed to turn black at 72.0°, however, some of the complex crystals did not decompose until the temperature was at 86°. The complexes dissociate leaving behind a white solid (cuprous chloride) which appears black in the field of a microscope.

It is interesting to know that at 72.5° different crystals appear in the field and grow in the absence of a liquid phase. These well formed crystals melt at 94-96° although many of them disappear (sublime) before this temperature.

The alkyndiol (m.p. 94-96°) was used as taken from a sample given by Air Reduction Chemical Co..

Gilman, Bukhovetc, and Meilakh (62) have prepared a yellow platinous chloride complex containing 2,5-dimethyl-3-hexyne-2,5-diol and pyridine as the ligands. This complex represents the only known platinous chloride-alkyne compound even though Chatt (51) has attempted the preparation of similar complexes involving simple disubstituted alkynes.

System; Cuprous Chloride and 1-Butyne. In a tared ampoule 0.836 g. of cuprous chloride dissolved in 1.6 g. of 1-butyne to give a clear colorless liquid. No precipitate or gas was formed during the solution of the cuprous chloride. Clear colorless crystals were first observed when the ampoule was allowed to stand at -17° for an hour. The crystals readily dissolved when the ampoule was warmed to 0°. The solubility of the crystals in excess 1-butyne is considered to be quite high since a large quantity of crystalline material had been present at -17°.

It is inferred from the general properties of the system that the crystalline product is a molecular complex similar to the cuprous halide-disubstituted alkyne complexes whose existence had been demonstrated earlier. This inference is substantiated by the quantitative recovery of white cuprous chloride from the ampoule.

1-Butyne was prepared by Helmkamp (63) and was purified by distillation from liquid nitrogen temperature to a flask cooled in a dry ice-acetone mixture.

Fig. 52 Cuprous chloride-1,6-heptadiyne crystals, mother liquor (ampoule, x100).

System; Cuprous Chloride and 1,6-Heptadiyne.* The stable tabular colorless complexes formed by this system can be prepared by warming cuprous chloride with excess alkyne in the presence of air or mixing the components and allowing them to stand over night. Crystals grown in an ampoule by this latter method are shown in Fig. 52.

The dry crystals are stable for at least 24 hours if kept in a stoppered container, and in the presence of excess liquid they are stable in air for several months. After this period of time decomposition is indicated

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* The 1,6-heptadiyne and 1,8-nonadiyne cuprous halide systems were studied at the suggestion of Professor Davidson, who considered the possibility of their chelating properties. The alkynes were taken as supplied by Farchan.

by a brown precipitate. When the crystalline complex is warmed in the capillary of the melting point apparatus decomposition starts at 107° and is quite definite at 110° and at 116° only a few crystals retain their shape ("B" at 25°).

System; Cuprous Bromide and 1,6-Heptadiyne. Colorless complex crystals of this system may be prepared as described for the chloride analogue and are similar in their stability. When first grown from solution the complex appears as clusters of fine needles, however, upon standing, well developed crystals like those shown in Fig. 53 and 54 are formed.

The decomposition range of the crystalline complex in the melting point apparatus ("B" at 25°) is 57-58°.

System; Cuprous Chloride and 1,8-Nonadiyne. Colorless needles are formed upon cooling to room temperature a warm solution of cuprous chloride in 1,8-nonadiyne. The isolated complex may be handled in a normal manner for short periods of time without danger of decomposition. On a hot-stage melting point apparatus the crystals decompose in the range 97-104°.

System; Cuprous Bromide and 1,8-Nonadiyne. The colorless needles of this system are very similar to the chloride analogue. However, their preparation is best achieved by mixing the components and allowing them to stand 24 hours.

On a hot-stage melting point apparatus they decompose

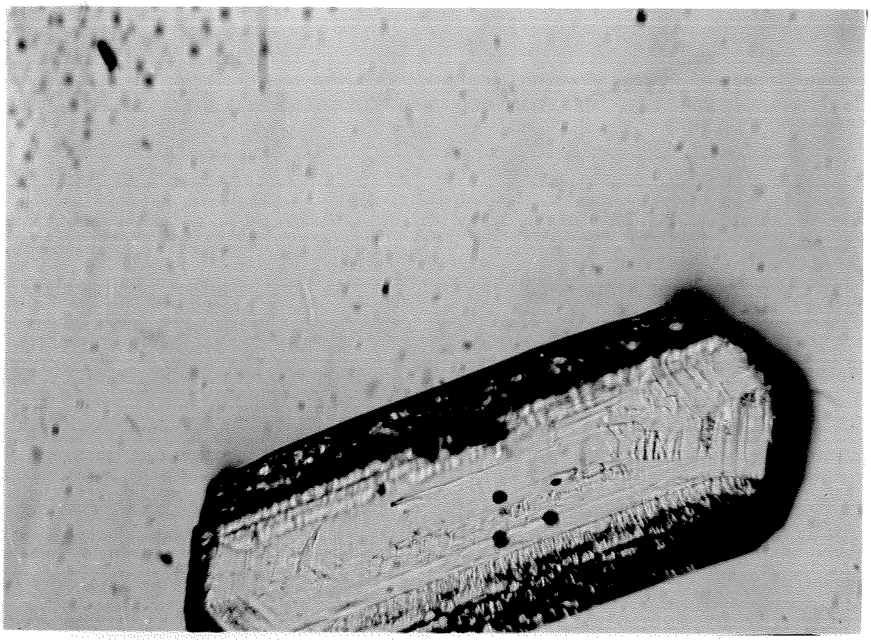

Fig. 53 Cuprous bromide-1,6-heptadiyne crystalline complex, mother liquor (ampoule, x100).

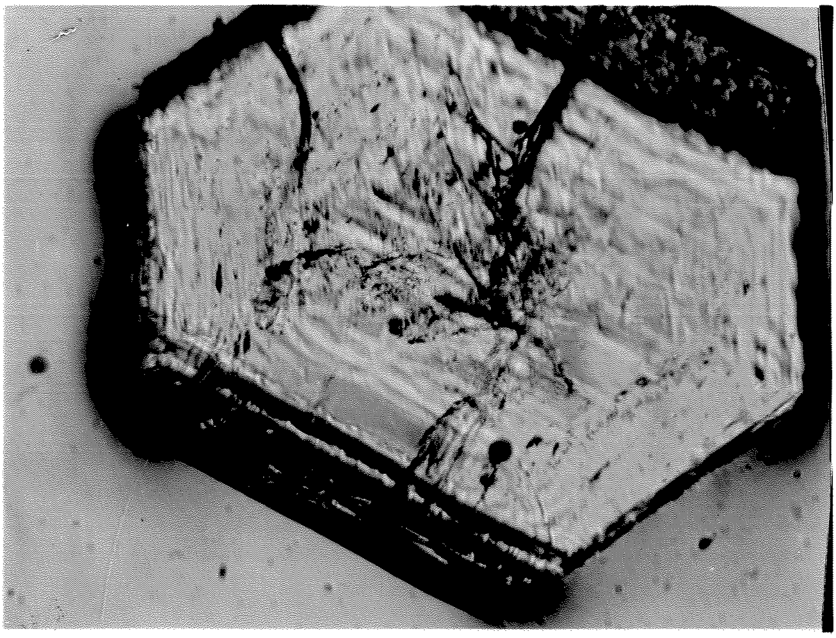

Fig. 54 Cuprous bromide-1,6-heptadiyne crystalline complex, mother liquor (ampoule, x100).

in the range 68-78°. However, at 78° a colorless liquid suddenly appears and then disappears.

System; Cuprous Chloride and 1,3-Butadiene. Gilliland, Bliss, and Kip (12) report that the color of the cuprous chloride-butadiene complex is yellow. This complex has been prepared in three different ampoules in this laboratory starting with white cuprous chloride and commercial* butadiene. Although the outward appearance of the complex in the ampoules was pale yellow, crystals on the sides of the ampoules were colorless. A microscopic examination (x100) at room temperature also revealed the presence of clear colorless needles. These were sometimes associated with aggregates of green material. The liquid in equilibrium with the crystalline complex is colorless and readily plates zinc strips with copper. The green material observed is considered to be an impurity.

System; Cuprous Halide and Acetonitrile. As noted by Naumann (64) solutions of cuprous chloride and cuprous bromide in acetonitrile are unstable in the presence of air. Concentrated solutions of cuprous chloride yield a flocculent brown precipitate in 2 to 3 minutes. The cuprous bromide acetonitrile solutions are somewhat more stable in air; decomposition occurs in about 30 minutes. Cuprous iodide solutions do not decompose in this manner.

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* Mathieson Co.

Under oxygen-free conditions the solutions are clear and colorless. When sufficient cuprous halide is present, colorless crystalline complexes are formed. The cuprous chloride- and cuprous bromide-acetonitrile complexes have been known for some time (65). The conditions and results of their composition analyses according to the method given on page 83 are indicated in Table 11. The results, i.e., that they exist as 1-to-1 complexes, are the same as those obtained previously by Morgan (66). The cuprous iodide-acetonitrile complex has not been previously reported.

In contradistinction to their solutions, the solid cuprous halide complexes freed from liquid are stable in the presence of air for relatively long periods of time, i.e. the production of the brown oxidation product is not observed. However, the colorless compounds are easily dissociated under low acetonitrile pressure into their components. A very thin film of cuprous halide is formed on their surfaces when they are allowed to remain in an unstoppered tube in air. In the cuprous bromide-acetnitrile complex this film imparts to the crystals a golden hue. The bromide complex is relatively more stable in the presence of air than the cuprous chloride-or iodide-acetonitrile complexes. This relative stability is also reflected in their decomposition points. When the dry solid complexes are prepared in the capillary of the melting point apparatus (see page 43 and Fig. 2) they decompose under the following conditions:

(i) cuprous chloride, 46-60°, bulb "B" at 25°,

(ii) cuprous bromide, 75.5-76.8°, "B" at 25°,

(iii) cuprous bromide, 57.5-59.2°, "B" at 0°,

(iv) cuprous iodide, 33.1-39.5°, "B" at 25°.

From a knowledge of the decomposition points of the cuprous bromide-acetonitrile complexes at different ligand pressures (i.e., bulb "B" at different temperatures) it is not possible to calculate a reliable heat of dissociation since the data do not give equilibrium information, even though the decomposition points are reproducible. In the case where the dissociation vapor pressure curves are known, the experimental decomposition temperature has been found to be 5-10° above that calculated for equilibrium conditions. Nevertheless the experimental decomposition temperature as determined with the melting point apparatus has been found to be an index of the relative stability of the complexes. Hence, the stability of the cuprous halide-acetonitrile complexes as a function of a cuprous halide decreases in order CuBr > CuCl > CuI. The thermal decomposition of the cuprous iodide-acetonitrile complex is frequently associated with the appearance of a bright red residue similar to that described in a footnote on page 39. This red decomposition product redissolves in excess acetonitrile to give a colorless solution.

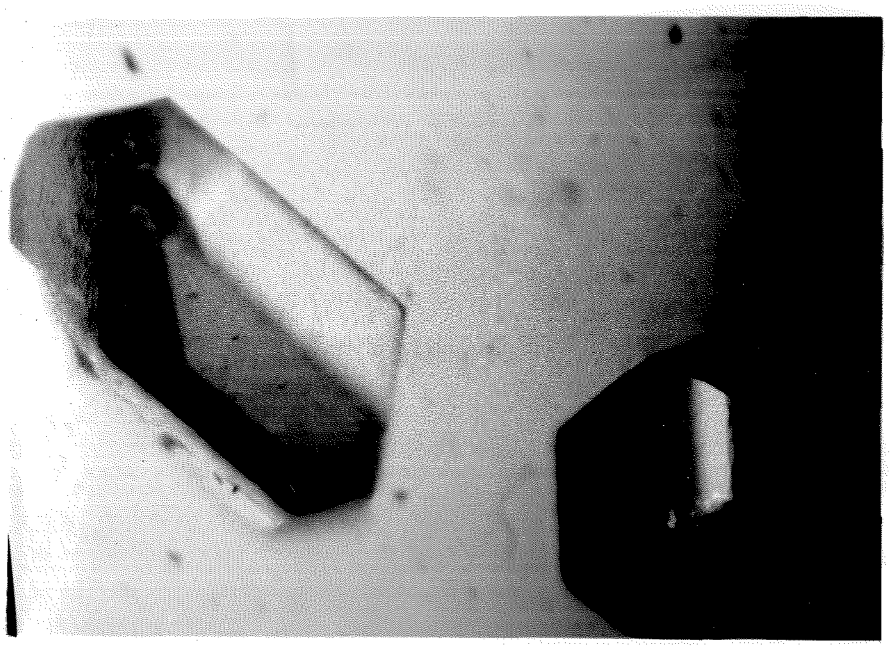

Fig. 55 Cuprous chloride-acetonitrile crystals in mother liquor (ampoule, x100).

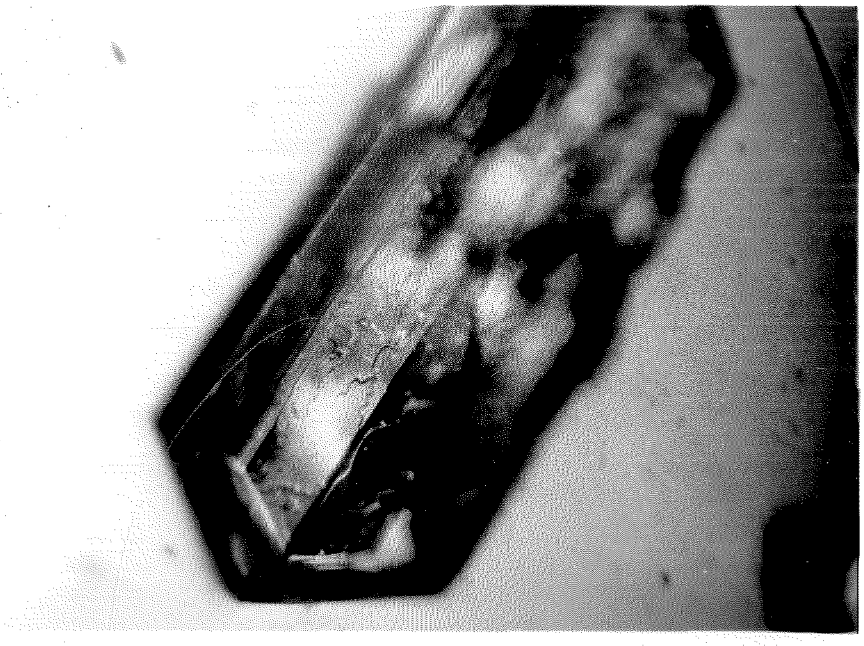

Fig. 56 Cuprous chloride-acetonitrile crystals in mother liquor (ampoule, x100).

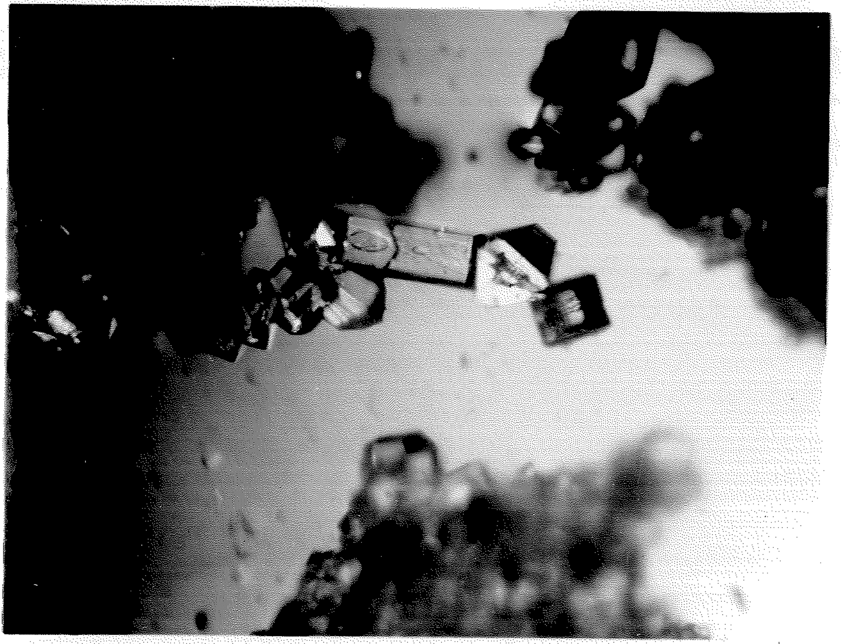

Fig. 57 Cuprous bromide-acetonitrile crystals grown from solution in the absence of air, photographed in air,(x100).

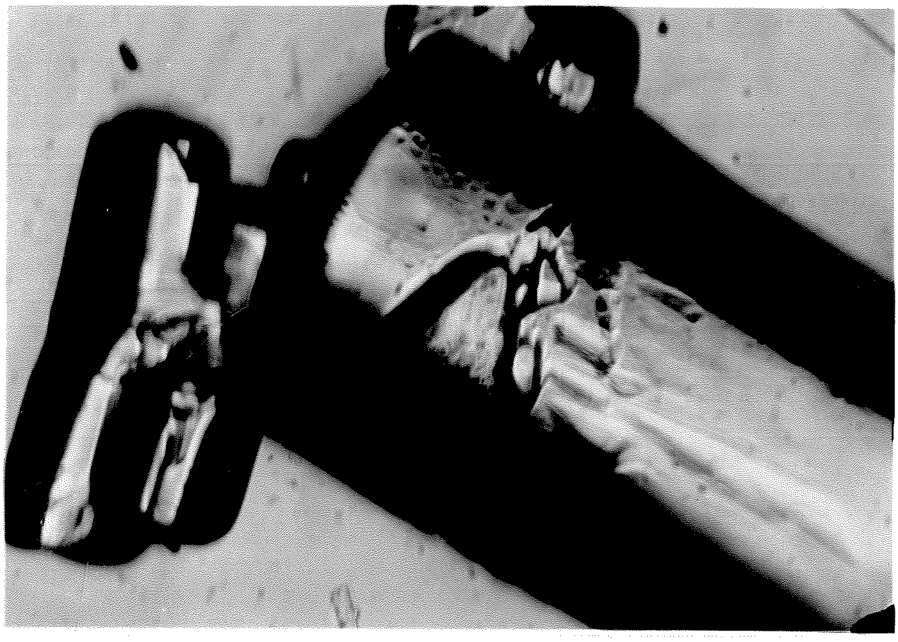

Fig. 58 Cuprous bromide-acetonitrile crystals in mother liquor (ampoule, x100).

Fig. 59 Cuprous iodide-acetonitrile complex crystals enclosing buff cuprous iodide; mother liquor (ampoule,x100).

Photomicrographs of the cuprous halide complexes have been taken. Fig. 55 and 56 illustrate the cuprous chloride complex crystals formed on standing at room temperature in a sealed ampoule. The cuprous bromide-acetonitrile complex crystals obtained from solution when excess solvent is slowly distilled off are illustrated in Fig. 57. Much larger crystals, as indicated in Fig. 58 are formed in sealed ampoules in the presence of excess ligand. Clear colorless crystalline complexes of cuprous iodide and acetonitrile have been observed to form around the amorphous buff colored cuprous iodide aggregates. This is illustrated in Fig. 59 where the dark centers of the otherwise clear crystals are particles of cuprous iodide. The encapsuled cuprous iodide decreases in size as a function of time. One or two days after the sealing of the ampoule very few complex crystals contain enclosed cuprous iodide.

System; Cuprous Cyanide and 3-Hexyne. Reagent grade cuprous cyanide and 3-hexyne react in a sealed ampoule in one to four days to give well formed colorless crystals. In different ampoules two different crystalline forms of the product have been observed. However, there is no reason to believe that the two compounds are different since they behave in a very similar fashion. Both forms are easily decomposed at low hexyne pressure or high temperature (i.e. less than 100°) and both appear to be relatively insoluble in excess alkyne. Photomicrographs of the habits are shown in Fig. 60 and 61. The needles were grown in a small ampoule (8 mm. diameter) which was three fourths filled with liquid. The tabular crystals were grown in a larger ampoule (12 mm. diameter) which contained a much smaller relative volume of the alkyne. With the exception of the columnar crystal and the needlelike crystal in Fig. 61 coexistence of the two forms has not been observed even though the ampoules have been inspected at various times for six months.

When bulb "B" of the melting point apparatus is at 25° and the capillary containing dry cuprous cyanide-3-hexyne crystals is in a melting point bath the following observations were made when the temperature of the bath was increased;

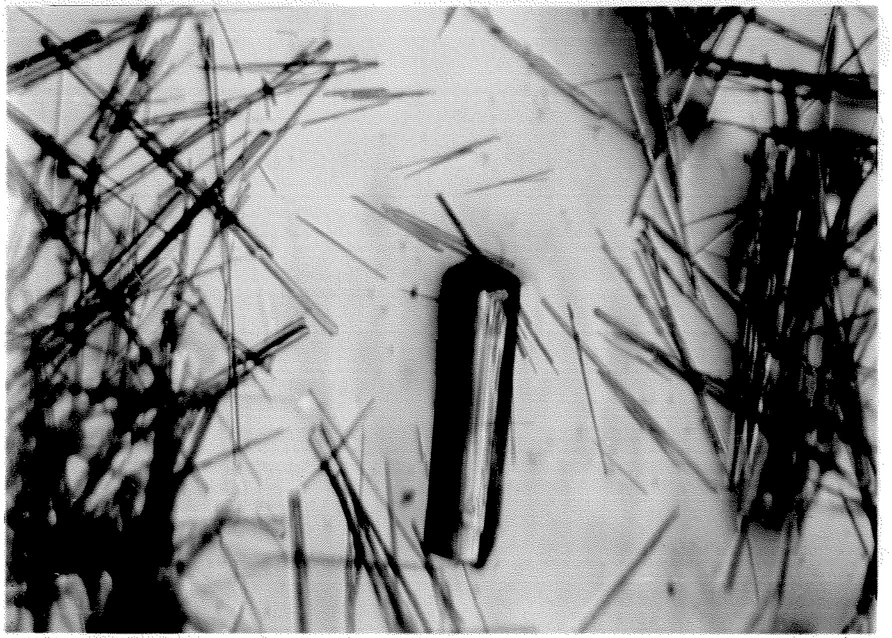

Fig. 60 Cuprous cyanide-3-hexyne complex crystals, mother liquor (narrow ampoule, x100).

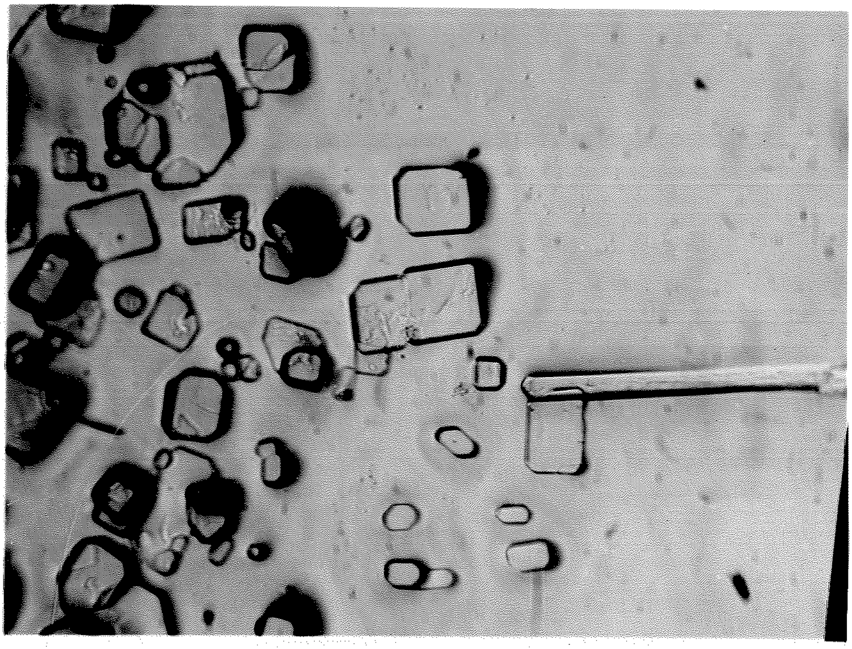

Fig. 61 Cuprous cyanide-3-hexyne complex crystals, mother liquor (wide ampoule, x100).

(i) at 40° clear colorless reflecting crystals were present,

(ii) at 40.6° a very thin film developed on the surfaces of the crystals,

(iii) at 43.4° the film is quite definite but the crystals still have their shape and most of the reflecting power,

(iv) at 44.3° the crystals are almost opaque due to the thickening of the cuprous cyanide film,

(v) at 45° most of the crystals are opaque and some have lost their shapes, and

(vi) at 46° reflected light is no longer observed.

System; Silver Chloride and 3-Hexyne. No complex formation has been observed in this system. However, the appearance of very thin clear laminae (ca. 2 mm. wide) have been noted when reagent grade silver chloride (lump form) was shaken in an ampoule with 3-hexyne for 24 hours. The quantity of the laminae increases with shaking. The laminae are without symmetry elements and are not decomposed when exposed to low pressures for long periods of time. In the presence of indirect sun light they become pale purple, and when heated do not decompose or melt below 320°. However, at 225° small black spots begin to appear in the laminae but do not increase in size. The recovered supernatant liquid did not plate a copper wire over night.

Silver chloride sealed in an ampoule with acetonitrile did not show this phenomenon even though the systems were treated in a similar manner. The laminae observed in the silver chloride 3-hexyne system are tentatively considered to be silver chloride. If this were so, then they are of some interest since silver chloride belongs to the cubic system.

<u>System</u>; <u>Cupric Chloride and 3-Hexyne</u>. Brown cupric chloride prepared by the dehydration of reagent grade $CuCl_2 \cdot 2H_2O$ in the vacuum system was sealed in an ampoule with 3-hexyne (<u>ca</u>. 1.5 ml.). The 3-hexyne, recovered from the solubility determination of the cuprous bromide-3-hexyne complex, had been treated with sodium. However, prior to the preparation of the cupric chloride 3-hexyne ampoule the 3-hexyne could have been contaminated with a small amount of water dissolved during a brief contact with air when the 3-hexyne was at a temperature lower than ambient.

A light brown color developed in the liquid when the ampoule was shaken for 24 hours. After 36 hours of shaking a change in the color of the solid was also noted, <u>i.e</u>. a small part of the solid was a dark brown. After two week's time most of the solid had changed to the darker form; the solution however was still a light brown. A few light green columnar crystals were also present.

The ampoule was opened and the contents examined. The brown color of the solution was not removed by filtration;

however, when the solvent was vacuum distilled, the color was not transferred. The refractive index of the recovered liquid was $n^{25}D$ 1.4110 while for pure hexyne $n^{25}D = 1.4090$. The recovered liquid had a new odor (similar to cinnamon) in addition to that of 3-hexyne.

The solid products were examined on a Kofler micro hot stage. The clear green crystals decomposed at 78.5° to a brown opaque mass; $CuCl_2{\cdot}2H_2O$ decomposed under similar conditions at the same temperature. The dark brown product which did not appear crystalline changed in character at approximately 348° to form a different transparent brown solid.

An ampoule was prepared which contained a zinc strip in addition to the contents (cupric chloride and 3-hexyne) as prepared above. The metallic zinc was plated with copper, and the liquid developed a dark brown appearance upon shaking a few hours. After several weeks a microscopic examination of the ampoule indicated the presence of two liquid phases, a colorless liquid in small quantities which deposited a white solid when evaporated with hot wire and a dark brown liquid which yielded a very dark solid in addition to the white deposit.

Pure 3-hexyne from storage and cupric chloride in an ampoule react slowly (7 days) to give a very light brown solution with a simultaneous production of a dark brown solid. All the cupric chloride was converted into the dark brown solid in two week's time.

System in which Complex Formation was not observed.

The following compounds sealed in oxygen-free ampoules for more than a year have not reacted,

$CuCl$, 2-heptynoic acid;

CuI, 1,6-heptadiyne (4 months);

$CuSCN$, 3-hexyne;

Cu_2O, 3-hexyne;

$AgCl$, 3-hexyne;

CuO, 3-hexyne;

$CuCN$, Acetonitrile.

3-Hexyne reacts with air in a short time (24 hours) in the presence of cuprous iodide and cuprous thiocyanate to give non-volatile pale green liquid products. The inorganic components have not been observed to form complexes with the alkyne. 3-Hexyne in the presence of cuprous cyanide also reacts with air to give a similar product.

R. SOME CONCLUDING REMARKS.

General Properties of the Cuprous Salt-Alkyne Complexes. All of the investigated alkyne complexes which contain cuprous salts have been found to be colorless and crystalline, and they are easily dissociated or melted except in certain cases where additional effects may be operative. The exceptional stability of the crystalline cuprous chloride-3-heptyn-1-ol complex may be attributed to the presence of the β-hydroxyl group. It appears that when this functional group is α to the triple bond additional stability is not derived from its presence. The melting points of the complexes and their solubilities in excess alkyne are definitely related to the position of the triple bond in the alkyne. High solubility and a low melting point of the complex are associated with those alkynes which have the triple bond near a terminal position.

The stability and high decomposition temperature of the cuprous chloride diyne complexes can be easily interpreted in terms of the nucleus model for the crystalline complex. Since two nuclei could be bound together by one diyne it is possible that the crystalline complexes consist of giant molecules. If both triple bonds of a diyne were always associated with metal atoms of the same nucleus then a low melting point would be expected even though dissociation of the melted complex would be at a much higher temperature.

In contrast to the argentation studies (23) involving aqueous silver nitrate solutions substitution of the hydrogen atoms α to the triple bond by methyls does not seem to decrease the stability of the cuprous salt complexes.

A study of complexes in solution indicates that they absorb in the infrared and the ultraviolet.

α and β Crystalline Phases. Further evidence corroborating the existence of the hypothesized α and β crystalline phases has not been obtained from the study of solutions of complexes or from the preliminary examination of the infrared and ultraviolet absorption spectra of solutions containing the alkyne complexes. However, this is not surprising as the presence of more than one species in solution is considered established.

A Brief Comparison of the Cuprous Salt-Alkyne Complexes with Those of Other Known Ligands. A number of unsaturated functional groups are known to date to form easily dissociated addition compounds with cuprous salts. Some of these are carbon monoxide as in $CuCl \cdot CO \cdot H_2O$ (4), alkyl isonitriles as in $CuCN \cdot RNC$ (67), aryl isonitriles as in $CuCl \cdot (C_6H_5NC)_n$ where n = 1,2,3, and 4 (68), nitriles as in $CuCl \cdot CH_3CN$, olefins as in $2CuCl \cdot C_4H_6$, acetylene as in $2CuCl \cdot C_2H_2$ (6), and the mono-and disubstituted acetylenes. All of these solid, well crystalline, easily dissociated complexes have an additional feature in common. They are colorless.

The reported colored cuprous salt complexes similar to these must be attributed to impurities or to phenomena other than the interaction of the copper atom with a single unsaturated center.

The Complex Bond. The most convincing formulation of the complex bond responsible for the existence of the cuprous halide-alkyne complexes is that proposed by Dewar (69) for the silver and cuprous salt-olefin complexes and elaborated on and extended by Chatt (70) to the platinous chloride-olefin complexes. Briefly, Dewar's formulation of the complex binding is as follows: two types of bonds are formed between the metal and the olefin. The first is designated as a σ bond and corresponds to the interaction of the electrons of the filled $\pi_z 2p$ molecular orbital with the unfilled s orbital of the metal. This can be reinterpreted as the interaction of the polarizable electrons of the unsaturated hydrocarbon with a positive charge. Dewar's second bond, a π-type bond, requires that the donor and acceptor roles of the components be interchanged. In this case the electrons of the filled d orbitals of the metal interact with the vacant antibonding molecular orbitals of the olefin. Except to say that these considerations place the metal in the plane which is the perpendicular bisector of the line joining the two olefinic carbon atoms there is little reason to parrot their discussion further. This model readily leads one to the following observations not mentioned by the above authors;

(i) In the first place it is clear that the areas of maximum overlap are not centered about the carbon-metal direction, *i.e.* electronic distributions comparable to those of ordinary σ bonds are not formed.

(ii) Since Dewar's σ bond is probably responsible for the major part of the interaction of the components and since this bond is not highly localized, the force constants for the metal component are probably unusually low.

(iii) As a crude approximation which ignores the origin of the electron responsible for the formation of the different bonds (σ -and π-type bonds) the bonding orbital for the complex may be visualized as a thick fan emanating from the metal atom.

(iv) As in the case of the postulated excited state of acetylene (71) the presence of the d electrons in the antibonding molecular orbitals in an alkyne will be expected to exert a repulsive force on the σ electrons of the adjoining single bonds. This force can be relieved by the rehybridization of the acetylenic σ bonds. Hence, for the 2-butyne complexes the carbon structure of the alkyne would tend toward that of cis-2-butene. Other possibilities, however, cannot be excluded. It will be observed that this complex is different in its configuration from that proposed for the silver ion cis-2-butene complex (72). In the alkyne complex the metal atom would be in the plane of the four carbons. In the olefin complex the metal is visualized as being above the plane of the carbons interacting with the π electrons of the double bond. Some rehybridization of all the σ bonds of the unsaturated carbon atoms would also be expected. In the cis-2-butene complexes the terminal carbon atom separation would be decreased because the rehybridization of the olefinic carbon atoms would tend to make them tetrahedral in their valence bond directions.

Relative Stability of the Cuprous Halide-Disubstituted Alkyne Complexes. Dissociation vapor pressure measurements at 25° (Table 19) and experimental dissociation temperatures indicate that the cuprous chloride-alkyne complex is more stable than the bromide analogue. No evidence for the formation of possible cuprous iodide-alkyne complexes has been found. Hence, the affinity of cuprous halide for an alkyne decreases in the order $CuCl > CuBr > CuI$.

Following Pauling (73) this order can be interpreted as the effect of the electronegativity of the halogen on the binding capacity of the copper. As the electronegativity of the halogen increases the ionic character of the cuprous halide bond is expected to increase; this would make available an increased bonding capacity of copper for the ligand.

An alternative though less probable explanation involves the use of the copper d orbitals. As mentioned above Dewar suggested that the d orbitals of the metal interact with the antibonding orbitals of the carbon-carbon double bond in the metal salt-olefin complexes. The variation of the cuprous halide affinity for the triple bond could be accounted for if the stability of the cuprous halide-alkyne complexes was strongly dependent upon a similar effect (which probably exists). The explanation, however, involves two assumptions:

(i) the availability of the d electrons of copper is small and

(ii) the d character in the cuprous halide bond increases with the molecular weight of the halogen.

The first assumption is reasonable since it is doubtful that sufficient energy is available from the formation of the complex bond for the promotion of a 3d electron to a higher orbital, and the second is reasonable since inner d-character in the cuprous halide bond would increase overlap because of its diffuse nature and would add to the stability of the bond in a manner proportional to the size of the halogen. Hence, the higher the atomic weight, the more d character would be in the cuprous halide bond and the less available to interact with the ligand's unoccupied orbitals.

Intermediate Complex Bonds. As the ligands for cuprous salts are considered in the order of CO, RNC, RCN, HCCH, RCCH, and RCCR, it is clear that the associated metal ligand bond changes its type from the ordinary σ bond in which the metal is colinear with the unsaturated atoms of the ligand to Dewar's π complex bond as in the disubstituted alkyne complexes where obviously the σ bond as above is impossible. With the first three mentioned ligands both types of complex bonds are at least conceivable. Is there then, a complex bond which is intermediate between the two extreme types, i.e. where the metal atom is neither colinear with the unsaturated atoms nor in the plane bisecting and perpendicular to the bond between the unsaturated atoms? And if so, for what ligands should this intermediate type bond be important? It is likely that such a complex bond does not exist for the 1-to-1 complexes. However, for the more complicated crystalline complexes such as $2CuCl \cdot C_2H_2$ and $Ag_2C_2 \cdot 6AgNO_3$ (21) this intermediate bond is probably important.

Final Consideration. Cuprous chloride, cuprous bromide, cuprous iodide, and cuprous cyanide have been shown to have the ability to react with known ligands. It appears, however, that the relative complexing affinities of these cuprous salts are interchanged depending upon the ligand. Observations concerning three different ligands will be noted;

(i) The present study has demonstrated the existence of the crystalline addition compounds of 3-hexyne with cuprous chloride, cuprous bromide, and cuprous cyanide. A complex of cuprous iodide with 3-hexyne has not been observed under any condition .

(ii) Acetonitrile has been shown to react with cuprous chloride, cuprous bromide, and cuprous iodide to form addition compounds, but not with cuprous cyanide.

(iii) Absorption studies by Manchot and Friend (74) have indicated that carbon monoxide is absorbed by the cuprous halides but not at all by cuprous cyanide. They have shown that the ability of the cuprous halide to absorb carbon monoxide decreases as the atomic number of the halide increases. As mentioned above, the same order exists for the alkyne complexes but not for the acetonitrile.

It appears then, that alkyl isonitriles and 3-hexyne are stronger ligands than acetonitrile and carbon monoxide for cuprous cyanide; but for cuprous iodide, acetonitrile and carbon monoxide are better ligands than 3-hexyne. The observed reversal in the apparent binding strength of the ligands is probably related not so much to the strength of the complex bond as to energetics of other factors such as the mode of packing in the crystalline state. The influence of other factors on the various kinds of heats of dissociation for the cuprous halide-alkyne complexes is quite apparent ($\Delta h_{Dis.}$ Table 19; Δh_L, Table 20). Familiarity with the complexes formed is not sufficient without detailed structural knowledge to permit clarification of the phenomena responsible for these discrepancies.

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PROPOSITIONS

1. It is proposed that hydrogen bonding with the carbon-carbon triple bond be studied in non-polar medium by infrared spectroscopy. Possible rehybridization of the bonds associated with the acetylenic carbons resulting in a non-linear carbon structure of 2-butyne in the methanol-2-butyne complex should receive special attention in view of the proposed (Dewar) structure of the silver ion-olefin complex.

J.S. Dewar, Bull.Soc.Chim.Fr., 18, C79 (1951).

2. It is suggested that the so-called strain energy of cyclic and acyclic compounds be studied as a function of partial ionic character.

3. An experiment comparable to the famous one of A.Stern and W.Gerlach would be of special interest in the study of free radicals, especially since an aggregate of non-combining free radicals could conceivably be obtained.

O.Stern, Zeits.f.Phys., 7, 249 (1921),
W.Gerlach and O.Stern, Zeits.f.Phys., 8, 110 (1921), 9, 349 (1922),
M.Deutsch, Phys.Rev., 82, 455 (1951).

4. The dropping mercury electrode as used in polarographic analysis introduces an unessential oscillation in the trace of the diffusion current versus applied voltage. This oscillation can be removed by the use of sintered glass ware. The form of the electrode proposed is a hollow cylinder of sintered glass joined at either end by barometric capillary tubing. Pure mercury under a small pressure difference is to be passed through the sintered hollow cylinder when the electrode is immersed in the solution to be analysed. This electrode has several advantages:

(i) The mathematics of the situation is greatly simplified over that for the dropping mercury electrode since diffusion is radial with respect to the thin mercury column.

(ii) The solution can be stirred without disturbing the processes in the vicinity of the electrode. Stirring is in fact advantageous in that it simplifies further the boundary conditions on the diffusion equation.

(iii) Density changes of the solution at the electrode are unimportant inasmuch as they do not introduce fluctuations in concentration.

(iv) Changes of the surface tension of the mercury are less important for this electrode than for the dropping mercury electrode.

I. M. Kolthoff and J. J. Lingane, "Polarography", Interscience Publishers Inc., New York, 1946.

5. It is common practice to reduce vapor pressure data to curves of the form

$$\log P = A/T + C$$

$$\log P = A/T + B \log T + C$$

where A, B, and C are constants to be determined by the method of least squares. This method of data reduction minimizes $\sum_i ((\log P_i)_{ex.} - (\log P_i)_{cal.})^2$.

In situations where the expected error in part of the pressure data is appreciable it may be desirable to minimize $\sum_i (P_{i_{ex.}} - P_{i_{cal.}})^2$ instead. This is most conveniently accomplished if the data are treated in the customary manner but are properly weighted. The weights to be used are proportional to $P_i/\sqrt{\log P_i}$.

6. There exist a number of compounds which offer the opportunity of studying unusual binding of ligands to metal atoms. One of these is the stable crystalline complex $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$.

It is not often possible to directly investigate an intermediate compound of a complicated reaction. A few such compounds exist in the solid state. One of these is obtained in the preparation of the starting material of the nitromalonaldehyde condensation. This intermediate is an orange-red crystalline product in the preparation of potassium nitromalonaldehyde from mucobromic acid and potassium nitrite.

The colored intermediate decomposes in a warm neutral aqueous solution to form carbon dioxide, hydrogen cyanide, and the colorless potassium salt of nitromalonaldehyde. The corresponding intermediate starting with sodium nitrite does not exist.

It is proposed that the crystal structure of these two compounds be initiated.

K.A. Hofmann and F.Z.Kuspert, Z.anorg.Chem., 15, 204 (1897).
H.B.Hill and C.R.Sanger, Ber., 15, 1906 (1882).
H.B.Hill and J.Torrey Jr., Am.Chem.Journ., 22, 89 (1899).

7. The value of conformal mapping in extending solutions of the two dimensional Laplace equation to related problems is very well known.

Similar extensions can be made for certain Sturm-Liouville equations with regular boundary conditions (*e.g.*, the two-dimensional Schrödinger wave equation). If, in the region R_z of the complex z plane the eigenvalues and the eigenfunctions of certain Sturm-Liouville problems with regular boundary conditions on curve C_z are known, then it is formally possible to determine the eigenvalues and eigenfunctions of related Sturm-Liouville systems in the region R'_w with regular boundary conditions on curves C'_w, where R'_w is related to R_z and C'_w and its associated boundary conditions are related to C_z and the original boundary conditions by a conformal mapping. The solution of the

unknown problem requires solving relatively simple bilinear simultaneous equations containing the eigenvalues of the known solution and integrals involving known functions.
R.V. Churchill, "Complex Variables and Applications", McGraw-Hill Book Co., Inc., New York, 1948, p.147 ff.

8. By redefining the code capacity of a code channel in a reasonable manner it is possible to demonstrate a correspondence between the formalism of information theory for a noiseless discrete system and the microcanonical ensemble of statistical mechanics.
C.E. Shannon and W.Weaver, "The Mathematical Theory of Communication", University of Illinois Press, Urbana, 1949.
R.C.Tolman, "The Principles of Statistical Mechanics", Oxford University Press, 1948, p.79.

9. W.King, E.H.Blaton, and J.Frawley have equipped an infrared spectrophotometer with a Digital Reader in parallel with the graphic reporter. This enabled them to record in binary code on punch cards the infrared spectra point by point. Their approach enabled them with the aid of a general purpose computer

(i) to have a permanent numerical record without the necessity of performing the time-consuming task of the visual reading of points from a graph,

(ii) to subtract spectra of known components,

(iii) to determine the absorption coefficients,

(iv) to analyze spectra of mixtures using non-linear variations of optical density with concentration (if necessary) at every wavelength instead of at salient peaks only, and

(v) to filter noise mathematically and to use narrower slit widths effectively.

It is proposed that the general policy be instituted to equip every automatic recording machine in the Gates and Crellin Laboratories with a digital reader outlet and to make available a suitable digital reader and general purpose computer services for routine problems.

The above authors based the coding of the measured intensity to binary digits on an 'arithmetic mean' scheme. If the coding is based on a 'geometric mean' then the percentage error of the intensity reading is minimized. Nevertheless it should be noted that the geometric coding method requires approximately two more binary digits than the 'arithmetic mean' coding method if similar percentage errors of maximum readings are expected for the two methods. G.W.King., E.H.Blaton, J.Frawley, J.Opt.Soc., 44,397 (1954).

10. A heuristic electrodynamic quantum mechanical explanation of the phenomenon of gravity can be given. F.K.Richtmyer, and E.H. Kennard, "Introduction to Modern Physics", McGraw-Hill Book Co., Inc., 1947, p.64.

11. It is proposed that the unreported carbon suboxide 'dione' ($O = C = C = O$) is a compound of more than ordinary interest. The synthesis of 'dione' should be seriously attempted and its properties studied. N.V.Sidgwick, "The Chemical Elements and their Compounds", Vol.I, Clarendon Press, Oxford, 1950, p.522.

12. The purification and isolation of compounds containing the triple bond may be facilitated through the formation of the cuprous chloride complexes. A qualitative study indicated that 3-hexyne can be quantitatively removed from carbon tetrachloride solutions by shaking the solution with cuprous chloride at -15°.

13. The present investigation of the cuprous halide alkyne complexes and the related problems is not considered complete. Two unsolved problems are especially immanent. One is related to the occurrence of unknown species in solution. The other concerns the nature of the complex bond. These problems are not unrelated. The size and shape of the alkyne molecule severely restrict the possible configurations of the complex polymers and probably influence the complex bond energy. The variation of the complex bond energy with the relative configuration of the two components is expected if the complex bonding metallic d orbitals have optimum relationships to the other directed metallic bonds. A judicious coordination of the following

suggested experiments may be especially advantageous in the determination of the nature of the complex species in solution:

(i) The solubility of cuprous halide in n-heptane solutions should be studied as a function of the alkyne concentration and as a function of temperature.

(ii) The determination of the average molecular weight of the cuprous halide in solution should be attempted by the method developed by S.M.Klainer and G. Kegeles for the ultracentrifuge.

(iii) The ultraviolet and infrared absorption spectra should be determined as a function of cuprous halide concentration, alkyne concentration, and temperature.

(iv) In view of the proposed participation of the metallic d electrons in the metal salt-olefin complex bond a determination of the magnetic susceptibility of the crystalline complexes or saturated solutions is warranted.

S.M. Klainer and G.Kegeles, J.of Phys.Chem., 59, 952 (1955).
L.Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, 1948, p.112 f.