

THERMAL ANALYSIS OF LIQUEFIED GASES

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I. INTRODUCTION

Thermal analysis of liquefied gases is based upon the experimental determination of the transition points of the cooling curves of given mixtures of two liquefied gaseous components in various known proportions. These transition temperatures are plotted *versus* the concentrations expressed in mole fractions to give a temperature-concentration phase-rule diagram.

A cooling curve is obtained by plotting the temperature *versus* the time when a two-component liquid system is caused to cool slowly to a temperature below its freezing point. As long as the system consists of a single liquid phase, the cooling curve will remain smooth and continuous. If a second phase appears, a sudden discontinuity in the curve will occur. If the new phase has the same composition as the liquid phase, the temperature will remain constant until all of the liquid phase has disappeared. If the new phase has a different composi-

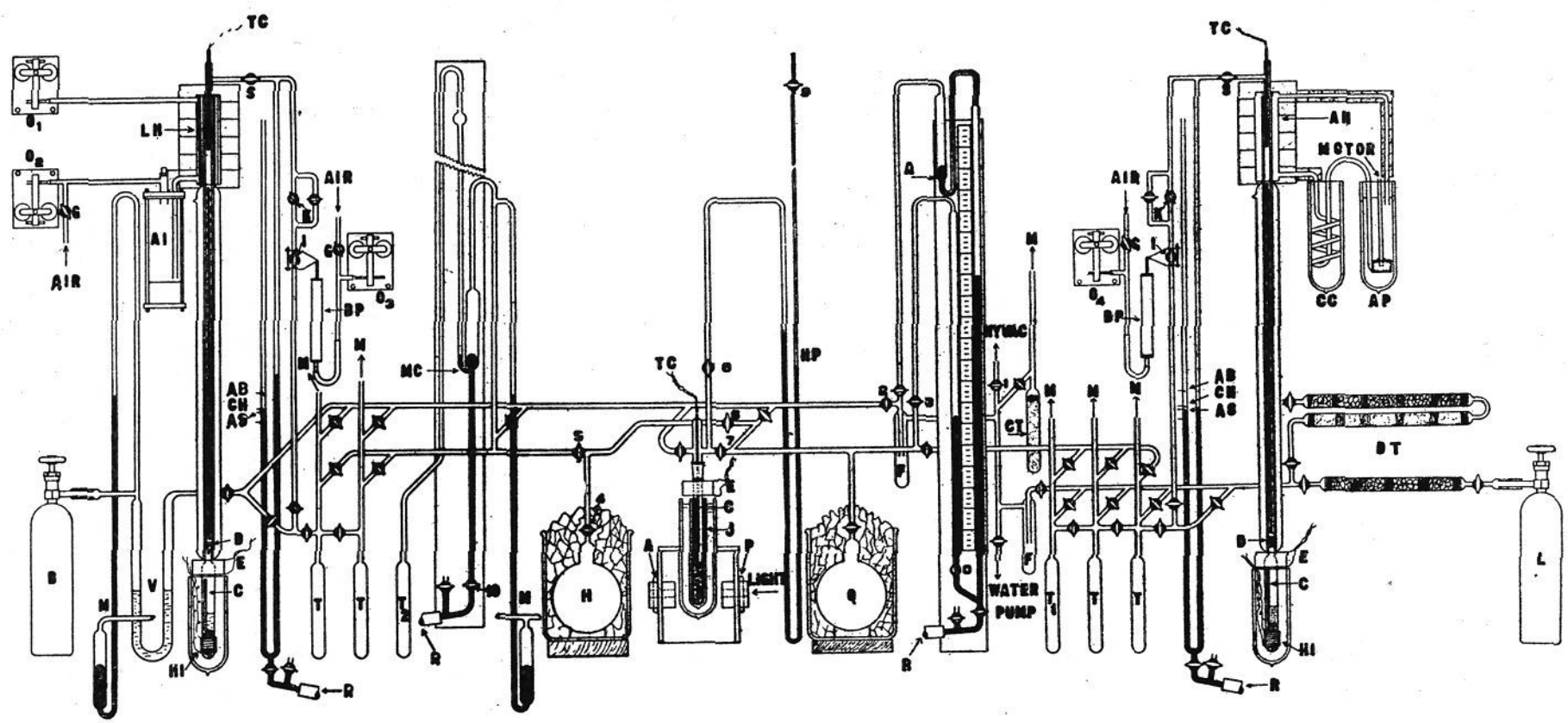


FIG. 1. Typical apparatus used for thermal analysis of liquefied gases

tion from the liquid phase, the cooling curve will undergo a change of slope due to the continuous alteration of the composition of the liquid phase as the temperature drops. Should a third phase form, the temperature of the system will remain constant until one of the phases has completely disappeared, and then give a second break in the cooling curve.

If the temperatures at which the transition begins on the cooling curves for various concentrations of the two components are plotted *versus* the concentration expressed in mole fractions or mole per cents, a temperature-concentration phase-rule diagram results.

In a temperature-concentration phase-rule diagram a compound displays a maximum, with a minimum usually occurring on each side of the maximum. This minimum temperature is usually called the eutectic point and represents the lowest temperature of freezing obtainable in any given system. This eutectic point will occur reproducibly at a definite concentration of the two components of the system in question and represents the freezing point not of a compound but of a mixture.

A compound can also be detected by the character of the cooling curve of a specific composition. A compound during freezing maintains a constant temperature, owing to the fact that the solid and liquid phases have the same composition. A liquid mixture when freezing merely gives a continuous change in the slope of the cooling curve, unless an enantiotropic transition takes place. Since such transitions proceed with accompanying energy changes, a discontinuity in the curve would occur.

The purpose of this paper is to make a critical survey of the investigations which have been published on the thermal analysis of liquefied gases, to correlate and evaluate the methods used, and to describe the binary systems reported.

In the thermal analysis of a gaseous system provision must be made in the apparatus for (a) the generation, purification, and storage of the gaseous components, (b) the establishment of the mole fractions, and (c) the determination of the freezing point of the mixture corresponding to these mole fractions. A typical apparatus for a thermal analysis is shown in figure 1 (17).

II. GENERATION, PURIFICATION, AND STORAGE OF GASES

A. GENERATION

It is desirable for the sake of convenience to obtain the gases to be used in a thermal analysis from cylinders. However, frequently this is not possible and it is necessary to generate the desired gas in the laboratory. The method of generation depends upon the gas desired, and generally consists in mixing the reactants in a generator flask attached to the bottom of a scrubbing tower. The gaseous products are taken off the top of the tower, led through a series of traps to condense the undesirable products, and condensed in the still pot of a fractionating column where further purification takes place (16).

B. PURIFICATION

The purity of the gases used is a primary prerequisite to a thermal analysis, because a slight trace of an impurity changes the freezing point of the pure

component in the same manner in which a small increment of the second component added to the first component would change the freezing point.

Some of the investigations of liquefied gaseous systems which have been carried out by thermal analysis should be repeated, because at the time at which they were studied efficient methods of gas purification had not been developed. Consequently, the reported freezing points of the pure components are from one to many degrees different from the values accepted at present. Frequently the investigator had to be satisfied with purification of the gases by ampule-to-ampule distillations. Rumold (39), working with boron trifluoride, found that thirty ampule-to-ampule distillations were necessary to obtain a constant value for the density of that gas.

Fractional distillation in a rectifying column is the common method for the purification of gases today. One fractionation with an automatically controlled column (16) is frequently sufficient to obtain a gas of high purity.

C. STORAGE

The purified gaseous components must be stored while fractions of them are used in the thermal analysis. The gases may be stored in either the solid, liquid, or gaseous state, the state used being dependent upon the type of vessel used,—glass balloon or glass ampule. If a balloon is used, the gas will be stored in the gaseous state at approximately atmospheric pressure; while if an ampule is used, the gas will be stored in either its liquid or its solid state depending upon the temperature of the refrigerant used.

If the gas is to be stored for a period of weeks, it is advisable to use a large glass balloon, thus eliminating daily addition of a refrigerant. For short-time storage this method is not practical, because the withdrawal of the gas from the balloon is time-consuming.

Storage of the gases in the liquid state is usually the best practice, because the difference between the coefficient of thermal expansion of the glass and the coefficient of thermal expansion of some gases from their liquid to solid states is so great that frequently ampules burst. Some gases cannot be kept as liquids by use of the common refrigerants and must therefore be kept as solids. When possible, it is advantageous to use carbon dioxide snow as the refrigerant in preference to liquid air, because the latter has to be replenished more frequently.

Precautions must be taken when storing gases to insure that they will remain pure during the storage period. The most likely source of contamination is a leak in the apparatus due to faulty stopcock lubrication. The stopcock grease used must be chemically inert toward the gases to be stored in the apparatus, must have a negligible vapor pressure, and must have a good bearing quality so that it will hold a vacuum over a period of weeks.

If a stopcock leaks, the gaseous component may become contaminated with either a condensible or a non-condensibile gas when liquid air is the refrigerant. If contamination is due to a non-condensibile gas, an error results in the establishment of the mole fractions as well as the lowering of the freezing point of the pure gas, providing the non-condensibile gas is soluble in the former. The

freezing point will be affected negligibly by the increase in pressure due to the presence of the non-condensable gas.

If a condensable gas, soluble in the pure gas being used, leaks into the pure gas, it may react with the latter to form a compound and thus either raise or lower the freezing point observed. If the condensable gas is soluble but non-reactive, the freezing point will probably be lowered. The freezing point in this latter case might be raised if a considerable quantity of the impurity leaked into the sample and if the freezing point of the impurity was much higher than that of the pure component. If the condensable gas is not soluble in the pure gas, two freezing points will be observed.

A condensable gas leaking into a pure gas may also cause its decomposition.

Another storage problem encountered is that decomposition or rearrangement may take place over a period of time, owing to surface catalytic action of dust, small glass particles, etc.

The above storage difficulties, excepting that due to decomposition to rearrangement, may be overcome by the use of an ampule, such as T_2 in figure 1, which has a mercury cut-off (MC) in place of the usual stopcock. After storage for a period of weeks the condensed gas in the ampule will have a blackish-gray color, which is due to the mercury condensed and not to an impurity.

The real problem is not purifying the gaseous components, but rather keeping them pure while the thermal analysis is being made.

III. EXPERIMENTAL METHODS FOR THE ESTABLISHMENT OF GASEOUS MOLE FRACTIONS

In a temperature-concentration phase-rule diagram accurate establishment of the composition of the various mixtures is imperative.

A. SYNTHETIC VOLUMETRIC METHODS

In the synthetic volumetric method, the mole fractions are made up to any desired value by adding small known volumes of one component to a known volume of the other.

Baume (3), one of the pioneer investigators in the thermal analysis of liquefied gases, used the synthetic volumetric method. This method, as modified and improved in the Morley Chemical Laboratory at Western Reserve University, will be described. The pure components, kept in storage ampules T_1 and T_2 (for boron trifluoride), are distilled into the calibrated flasks Q and H, respectively (figure 1), which are packed in cracked ice to maintain a temperature of 0°C . The pressures of the gases are measured on a Germann (23) baro-manometer O. To measure a quantity of the component stored in ampule T_2 , for example, all stopcocks except 3, 4, 5, and 6 are closed and the pure gas distilled through the mercury cut-off MC and through stopcock 5 into the evacuated space thus made available until the pressure is a little more than 1 atmosphere. Stopcock 5 is then closed and after the gas has cooled to 0°C ., as indicated by constancy of pressure, its pressure is read and recorded. Then stopcock 4 on the flask H is slowly closed. The gas in the manifold between stopcock 4 and the manometer is recondensed into the storage ampule T_2 by opening stopcock 5. The manifold

is now evacuated to the vapor pressure of the pure gas at liquid-air temperature. Flask H now contains a known volume of the gaseous component under a known pressure P' , at a known temperature 0°C . The flask stopcock 4 is then opened slightly and the desired amount of gas distilled into the freezing-point cell by opening stopcock 7. When the desired amount of the gas has been condensed, as indicated by the pressure drop on the manometer O, stopcock 7 is again closed. When equilibrium has been attained, the pressure P'' of the remaining gas in the calibrated flask H is read and recorded. Stopcock 4 on flask H is slowly closed and the gas in the manifold condensed into the freezing-point cell by opening stopcock 7. When all of the gas is condensed out of the manifold into the freezing-point cell, stopcock 7 is closed. Each time an increment of gas is added to the freezing-point cell, the above procedure has to be repeated.

Ruhemann and Lichter (37) used the same principle with a calibrated copper bomb and a baro-manometer in their study of the system nitrogen-oxygen.

The weight of the gas condensed in the freezing-point cell can then be calculated. The weight m of a gas of density L , at 0°C . and under a pressure p , in the volume in liters of the calibrated flask V , is given by the equation

$$m = \frac{pV}{760} L \left(1 + \frac{p - 760}{760} A_0^1 \right)$$

where A_0^1 represents the compressibility of the gas between zero and 1 atmosphere. The pressure p in the equation is equal to the difference in the pressure readings before and after some of the gas is condensed from the calibrated flask into the freezing-point cell.

Germann and Booth (25) have modified the above equation to

$$W = \frac{LV(P' - P'')}{(1000)(760)} = \frac{LVP^0}{(1000)(760)}$$

in which W is the weight of the gas condensed, P' is the pressure of the gas in the flask initially, and P'' is the pressure in the flask after condensation of some gas into the freezing-point cell, V is the volume of the calibrated flask in milliliters, and P^0 is the change in pressure caused by the condensation of some of the gas into the freezing-point cell. The molecular composition is desired instead of the weight, and according to the perfect gas law,

$$\frac{M_1}{M_2} = c \frac{P_1^0}{P_2^0}$$

in which M_1 and M_2 are the number of moles of gas 1 and of gas 2, P_1^0 and P_2^0 are their pressures, and c is the ratio of the volumes of the two calibrated flasks in which each of the gases was measured.

This equation, when corrected for the deviation of the two gases from the perfect gas law, becomes

$$\frac{M_1}{M_2} = c \frac{P_1^0 + \frac{P_1^0}{760} A_{1|0}^1}{P_2^0 + \frac{P_2^0}{760} A_{2|0}^1} = c \frac{P_1^0(760 + A_{1|0}^1)}{P_2^0(760 + A_{2|0}^1)}$$

in which $A_1']_0^I$ and $A_2']_0^I$ are the compressibilities of the respective gases between zero and 1 atmosphere. The mole fraction N_1 of gas 1 is given by the expression

$$N_1 = \frac{M_1}{M_1 + M_2} = \frac{cP_1^0(760 + A_1']_0^I)}{cP_1^0(760 + A_1']_0^I) + P_2^0(760 + A_2']_0^I)}$$

The corrective factors are small and may be neglected in most cases, especially if the gases are in approximately corresponding states at 0°C. and 1 atmosphere. In this case the calculation takes the simple form

$$N_1 = \frac{M_1}{M_1 + M_2} = \frac{cP_1^0}{cP_1^0 + P_2^0}$$

Another volumetric method which has been used is the measurement of the gases by a gas buret. Scheffan and McCrosky (40) measured each of the gaseous components in separate gas burets with mercury as the retaining fluid. Wheat and Browne (46) used water-jacketed gas burets for each of their components, with mercury as the retaining fluid for methyl chloride and a saturated sodium chloride solution as the retaining liquid for chlorine. Booth and Willson (18) have found that increased accuracy can be obtained by using a double baroburet.

Bagster (1) used a graduated ampule as a liquid buret. By distilling out a given volume of gas and recording the change in volume of the liquefied gas in the calibrated ampule, he calculated the mole fractions from the liquid densities of the gases. Corrections were not made for the change in volume of the ampule with temperature, thus introducing some error. This method would be advantageous with gases which attack mercury. Biltz and Bräutigam (15) used a similar method.

B. SYNTHETIC GRAVIMETRIC METHODS

Gravimetric methods have not been as widely used as volumetric methods in the synthetic establishment of the composition of mixtures in the thermal analysis of liquefied gases, probably owing to the fact that volumetric methods are more convenient to use with gases.

van der Goot (27), working with the system chlorine-sulfur dioxide, condensed one component into a weighed reaction tube, sealed the tube, and weighed it. The tube was then opened, the other component added, and the tube resealed and reweighed. All weighings were made at the same temperature. By this method the mole per cent of the mixture was determined to ± 0.1 per cent when approximately equal amounts of the two components were added. With an excess of either component the accuracy was less.

IV. EXPERIMENTAL METHODS FOR THE DETERMINATION OF FREEZING POINTS

After the mixture of the two components has been made and its concentration in mole per cent is known, the cooling curve for the mixture must be determined in order to develop the temperature-concentration phase-rule diagram. The early workers in the field had to determine their cooling curves manually by periodically reading the temperature of their thermometers or thermocouples

and recording these temperatures and time intervals. Then it was necessary for them to plot the temperature *versus* the time in order to determine where their cooling curve changed slope or gave an abrupt break. This laborious and inaccurate method has now been superseded by the use of thermocouples with recording potentiometers.

The basic procedure for the determination of freezing points was established by Beckmann (14). He used a thermometer and magnetically operated vertical stirrer inside the freezing-point cell. The magnetic stirrer consisted of a metal ring held horizontally above another metal ring by platinum wire and connected to a top iron ring coated with platinum. His freezing-point cell was surrounded by a solenoid. When the electric current was intermittently applied, the stirrer rose and dropped in the freezing-point cell, thus stirring the liquid. The freezing-point cell was then immersed in a suitable refrigerating bath the temperature of which could be controlled. Agitation of the bath insured uniform cooling.

Baume (3) modified the apparatus by placing the magnetic stirrer of the Beckmann apparatus within the freezing-point cell. The stirrer used differed from Beckmann's metallic stirrer, being all glass with a piece of iron enclosed in the uppermost glass ring. A pentane thermometer which had to be calibrated for errors due to stem emergence was used. To obtain a slower rate of cooling Baume surrounded the freezing-point cell with a glass jacket, thus creating a dead air space between the cell and the liquid-air bath. To prevent the jacket from frosting and thus hindering vision of the cell, he put anhydrous calcium chloride within the jacket. However, experience has shown that this is not effective in preventing frosting.

Bagster (1) improved the procedure by controlling the rate of cooling by means of a petroleum ether bath which was cooled by liquid-air injections and was stirred by dry air.

Germann and Booth (25) increased the stirring efficiency of Baume's apparatus by using a glass-spiral stirrer with a piece of soft iron sealed inside the top of the stem. The vertical motion of the stirrer gave the liquid a swirling motion.

Coffin and Maass (21) recorded the temperature of the liquid-air-cooled petroleum ether bath in which the mixture in the freezing-point cell froze, by means of a platinum resistance thermometer in the bath. It has been the authors' experience that resistance thermometers are too slow in attaining equilibrium for use in the observation of freezing points.

Biltz and Bräutigam (15) used a stirrer of the Beckmann type and determined the freezing points by use of an aluminum-block thermostat. The block was divided into two halves, separated by a very narrow air space. A recess in one half was charged with liquid air as required to give the desired cooling rate. Two holes were drilled in the other half; one for a pentane thermometer to record the temperature of the block, and the other hole for the freezing-point cell. The cell had a glass inner tube, surrounded by a stirrer, which contained a fused-quartz resistance thermometer. Measurements were reported accurate to $\pm 0.5^{\circ}\text{C}$.

Booth and Willson (18) improved the technic of Baume by means of three

modifications: (1) Polarized light was used to establish the moment at which crystals first formed in the liquid mixture. The cell was placed between two polaroid discs so that a beam of polarized light passed through the liquid in the cell, with the result that the microscopic anisotropic crystals flashed as white particles in a dark field before they were visible to the unaided eye (see figure 2).

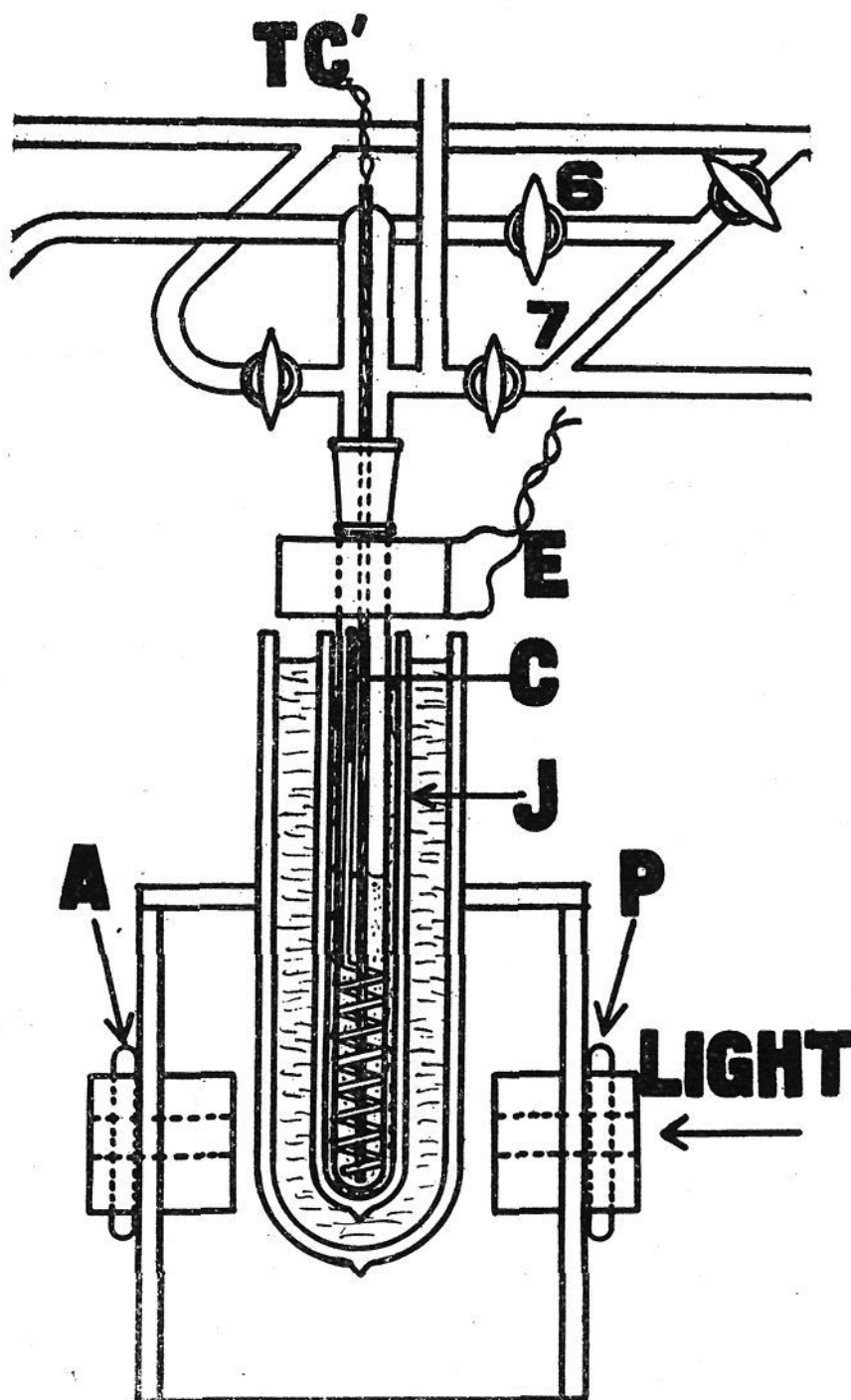


FIG. 2. The freezing-point cell

(2) The freezing point was recorded instantly in two ways on the chart of a Leeds and Northrup Micromax recording potentiometer connected to the multi-junction copper-constantan thermocouple in the freezing-point cell. A manually actuated electromagnetic pen indicated on the cooling-curve chart the time at which the crystals were first seen, and then the change of slope in the cooling

curve itself indicated the freezing point. However, in the vicinity of a eutectic the transition point is difficult to establish accurately by means of a cooling curve only. The use of polarized light and a magnetic pen enables the experimenter to establish transition points definitely at all compositions. (3) A vacuum jacket was used around the freezing-point cell.

In the method adopted in this laboratory the freezing-point apparatus shown in figure 2 (17) is used. The freezing-point cell contains a thin-walled glass thermocouple well TC, surrounded by an all-glass spiral stirrer with a piece of iron sealed in the top of its stem C. The stirrer is actuated by solenoid E. The rate of cooling is controlled by the small Dewar flask J, which is immersed in a quart Dewar flask containing liquid air. The quart Dewar flask is surrounded by a light-proof box through which passes a beam of light. The light passes through polarizer P and the freezing-point cell is observed through analyzer A.

The above methods are commonly employed for the determination of freezing points in the thermal analysis of liquefied gases. Two other methods have been reported: (1) The freezing points of mixtures of hydrogen chloride and nitric oxide were determined by use of a thermocouple in a conductivity cell (35). The freezing point was detected visually and checked when the conductivity dropped to zero. Difficulty was experienced in this method when the mole fraction approached 0.5, as both components tended to condense separately as pure solid phases. (2) Ruhemann and Lichter (37) determined freezing points in a vacuum calorimeter.

V. POSSIBLE SOURCES OF ERROR IN THERMAL ANALYSIS OF LIQUEFIED GASES

A discussion of the possible sources of error in the modified Baume method of thermal analysis of liquefied gases, now most generally used, is pertinent.

A. ERRORS IN THE DETERMINATION OF MOLE FRACTIONS

1. Pressure measurements

A great many specialized manometers have been built in an effort to eliminate the errors to which this instrument is subject, chief of which are the residual pressure in the barometric vacuum and the variations in the meniscus. Both objections would appear to be remedied in a barometer of wide bore, the vacuum chamber of which communicates with a vacuum pump; here capillarity no longer exercises an appreciable influence, the meniscus remaining perfectly flat except at the edges, and the quality of vacuum is under the experimenter's direct observation and control. Experience with this type of barometer has shown its superiority over the type composed of narrow glass tubing (23).

All pressure measurements are made, therefore, by a special U-type manometer, having a vacuum on one side which is established by a trap after the manner of the Germann manometer (23) (see A, figure 1). Both arms of the barometer are made of tubing of the same diameter. In this laboratory tubing of 14-mm. inside diameter has been found satisfactory. The manometer is filled by closing stopcock O and by opening stopcocks 2 and 3 (see figure 1). Both arms of the manometer are then evacuated, after which the mercury re-

servoir is raised until the mercury in the right arm rises in the capillary tubing. The reservoir is then lowered until the mercury level is at the base of the barometer. This operation is repeated slowly about twelve times to insure that no air will be trapped within the barometer. Then the mercury reservoir is raised until a small quantity of mercury has gone over into the trap A. Subsequent lowering of the mercury reservoir causes the mercury column to break in the capillary tubing, thus creating a vacuum over the mercury in the right arm. This lowering and raising of the mercury and subsequent overflow into A is repeated until no bubble is driven over. Stopcock O is then opened and stopcock 2 closed and the barometer is ready for use.

Since, in reading the absolute barometer, accuracy is required only to 0.5 mm., corrections for error due to capillary depression, for the thermal expansion of mercury and of glass, and for gravity become negligible.

When a gas in a calibrated flask is completely condensed into the freezing-point cell, a pressure change of about 760 mm. takes place. The pressure reading is easily accurate to 1 part in 760. The ratio of the volume of the calibrated flask to the volume of the freezing-point cell is usually such that the calibrated flask must be emptied twice in order to have sufficient liquefied gas in the freezing-point cell to give a reliable freezing point. The accuracy of the readings of the pressures is the limiting factor in the accuracy of determining the mole fractions because

$$N_1 = \frac{M_1}{M_1 + M_2} = \frac{cP_1^0}{cP_1^0 + P_2^0}$$

Assuming that the calibrated flask must be emptied twice to supply sufficient liquefied gas for a freezing point, the accuracy of the pressure readings for this component is 2 parts in 1520. The second component is then added in sufficient quantity to produce the desired mole fraction. If a pressure reduction of 100 mm. on the gas in the calibrated flask is assumed sufficient to introduce the desired quantity of the second component, the following calculation shows the accuracy of the mole fraction thus established:

$$N_1 = \frac{1520 \pm 2}{(1520 \pm 2) + (100 \pm 1)} = \frac{1520 \pm 2}{1620 \pm 3} = 0.938$$

The error is 3 parts in 1620, or 1 part in 540, and is equivalent to 0.2 per cent. The following table shows how the accuracy increases as succeeding increments of the second component are added until the flask is emptied. When a second flask full of the second component is required, the accuracy again drops.

P_1^0	P_2^0	N_1	ERROR IS 1 PART IN
<i>mm.</i>	<i>mm.</i>		
1520 ± 2	100 ± 1	0.938	540
1520 ± 2	200 ± 1	0.884	573
1520 ± 2	760 ± 1	0.667	760
1520 ± 2	860 ± 2	0.639	595
1520 ± 2	1520 ± 2	0.500	760

The greatest accuracy which can be claimed for mole fractions established by this procedure is 1 part in 500. The accuracy could be greatly increased by using a glass scale on the barometer in conjunction with a cathetometer, but such accuracy is not necessary for this purpose.

2. Volume measurements

The volume of the calibrated flasks is accurate to at least 1 part in 25,000 for 1-liter flasks. The method used for their calibration is that used by Germann and Booth (24).

3. Calibrated-flask temperature

The calibrated flasks are kept completely covered up to the stopcocks with cracked ice to insure that their temperatures are at 0°C.

4. Connecting manifold

The vapor pressure of the solidified gas in the freezing-point cell at liquid-air temperature results in a definite amount of the gas remaining in the connecting manifold. However, after each pressure reading the gas in the manifold is condensed into the freezing-point cell. Since the amount of gas left after this condensation is known from the vapor pressure of the gas at liquid-air temperature, condensation should be continued until the barometer reads this pressure. After the two gases are mixed, condensation must be continued until no further pressure change is noted on the absolute barometer per given time interval.

5. Compressibility coefficient

The coefficients of compressibility, $A_1|_0^1$ of some of the gases which have been used in thermal analysis investigations are not known. Any error introduced by not using these coefficients is negligible if the gases deviate only slightly from the perfect gas law or if the coefficients for the two gases are almost the same when the gases are in corresponding states.

B. ERRORS IN THE DETERMINATION OF FREEZING POINTS

1. Freezing-point cell diameter

Booth and Martin (17) found that the diameter of the freezing-point cell had no effect upon the freezing point obtained provided the thermocouple was sufficiently immersed. A cell having an outside diameter of 14 mm. proved to be the most practical.

2. Thermocouple

(a) *Type*: The copper-constantan thermocouple is used because it gives more millivolts per degree than other commonly used thermocouples (except iron-constantan), and because its calibration curve for liquid-air temperatures is better known (30).

Fine silk-covered 32-gauge wire is used to prevent error due to conduction of

outside heat to the junction. The junctions should be silver-soldered and arranged in the well above one another to prevent short-circuiting.

(b) *Calibration*: The thermocouple is usually calibrated against a platinum resistance thermometer in baths of melting ice, carbon dioxide snow, and liquid air. The actual values are then plotted parallel to the theoretical values (28), and this calibration curve is used to establish all experimentally determined temperatures. In the absence of a resistance thermometer the deviation can be established with satisfactory accuracy by the use of fixed points (43).

(c) *Immersion depth*: Booth and Martin (17) found that the top junction of a multijunction thermocouple should be immersed at least 4 cm. to give reliable freezing-point data at temperatures around -100°C .

(d) *Closeness to bottom of cell*: It was found that the distance of the bottom of the thermocouple from the bottom of the freezing-point cell had no effect upon the recorded temperature of the freezing point, provided the thermocouple was sufficiently immersed (17).

3. Recording potentiometer

A Leeds and Northrup Micromax recording potentiometer automatically records the cooling curve. It is accurate to 0.3 per cent of the millivoltage range. The recording potentiometers used in this laboratory have a range of 10 millivolts (0-10 and 5-15 millivolt ranges) and therefore are accurate to 0.03 millivolt. The recorder charts can be read to 0.02 millivolt. An optimum rate for the speed of the chart paper through the recorder is 8 in. per hour when the recorder is balancing every second and when the cooling rate is around 4°C . min.^{-1} (17).

4. Cooling rate

By use of a partially exhausted Dewar-type container for the freezing-point cell (J in figure 2), it was possible to maintain an optimum cooling rate of 3 to 3.5°C . per minute (17).

5. Viscosity

Later in the discussion of the various systems which have been studied by thermal analysis it will be noticed that sections of some of the phase-rule diagrams could not be determined, owing to high viscosity and to glass formation.

VI. SYSTEMS REPORTED IN THE LITERATURE

Only the binary systems of liquefied gases studied by thermal analysis in which *both* components are gases under standard conditions will be considered. In some of the systems a pressure in excess of 1 atmosphere has been created within the system, owing to the vapor pressures of the components. Only the salient data about each system will be given.

The method of classification is alphabetical. The components of each system are arranged alphabetically, as are also the systems. For example, the system composed of sulfur dioxide and boron trifluoride is listed as boron trifluoride-sulfur dioxide.

1. *Acetylene-hydrogen bromide (32)*

Acetylene, f.p. -81.8°C .; hydrogen bromide, f.p. -86.0°C . A eutectic occurred at 34.4 mole per cent acetylene and -126°C . No compounds were found. (See figure 3.)

2. *Acetylene-methyl ether (8)*

Acetylene, f.p. -81.5°C .; methyl ether, f.p. -138.0°C . Eutectics occurred at 64.5 mole per cent acetylene and -121.0°C ., and at 19 mole per cent acetylene and -152.0°C . The compound $\text{C}_2\text{H}_2 \cdot (\text{CH}_3)_2\text{O}$, f.p. -117.4°C ., was formed. The diagram is incomplete between 80 and 100 mole per cent acetylene. (See figure 4.)

3. *Allylene-hydrogen bromide (33)*

Allylene, f.p. -105.0°C .; hydrogen bromide, f.p. -86.0°C . Eutectics occurred at approximately 63 mole per cent allylene and -132°C ., and at approximately 24.5 mole per cent allylene and -138°C . The compound $\text{C}_3\text{H}_4 \cdot \text{HBr}$, f.p. approximately -126°C ., was formed. (See figure 5.)

4. *Ammonia-hydrogen sulfide (40)*

Ammonia, f.p. -78°C .; hydrogen sulfide, f.p. -83.5°C . Eutectics occurred at 95 mole per cent ammonia and -88°C ., and at 75 mole per cent ammonia and -18°C . The compounds NH_4HS , f.p. $+118^{\circ}\text{C}$., and $(\text{NH}_4)_2\text{S}$ were formed. The diagram was incomplete. (See figure 6.)

5. *Ammonia-methyl ether (11, 13)*

Ammonia, f.p. -78.3°C .; methyl ether, f.p. -137.6°C . Eutectics occurred at 62.5 mole per cent ammonia and -91.3°C ., and at 5 mole per cent ammonia and -141.1°C . The compound $\text{NH}_3 \cdot (\text{CH}_3)_2\text{O}$, f.p. -89.3°C ., was formed. (See figure 7.)

6. *Argon-boron trifluoride (18)*

Argon, freezing point not given; boron trifluoride, f.p. -127°C . Pressure-temperature diagrams for various mole fractions were determined, and from these data a temperature-concentration phase-rule diagram was made of the stabilized system by extrapolation of the temperature upward to a pressure sufficiently high to be above the decomposition pressure for all of the compounds found. Data were given for the compounds $\text{A} \cdot \text{BF}_3$, f.p. -128.6°C .; $\text{A} \cdot 2\text{BF}_3$, f.p. -127.6°C .; $\text{A} \cdot 3\text{BF}_3$, f.p. -128.3°C .; $\text{A} \cdot 6\text{BF}_3$, f.p. -128.3°C .; $\text{A} \cdot 8\text{BF}_3$, f.p. -128.4°C .; and $\text{A} \cdot 16\text{BF}_3$. Data were given for eutectics at 19.9 mole per cent argon and -129.7°C ., and at 30.0 mole per cent argon and -131.6°C . The phase-rule diagram shows eutectics at approximately 1.5, 8, 13, and 38.5 mole per cent argon. (See figure 8.)

7. *Argon-krypton (44)*

Argon, f.p. approximately -189°C .; krypton, f.p. approximately -157°C . Non-porous mixed crystals were formed. A smooth S-shaped curve was obtained. (See figure 9.)

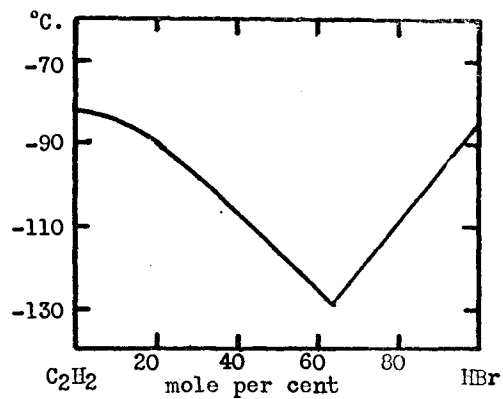


FIG. 3. Acetylene-hydrogen bromide system

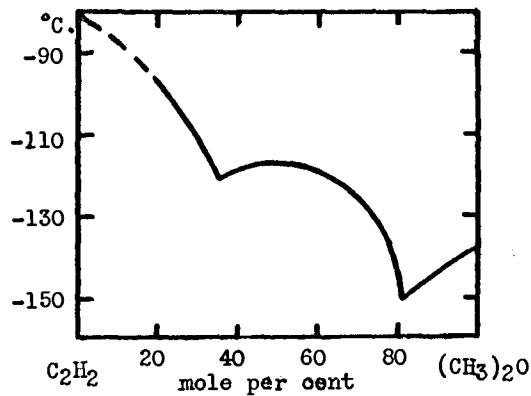


FIG. 4. Acetylene-methyl ether system

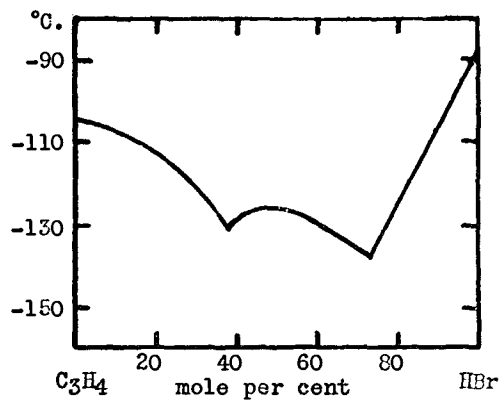


FIG. 5. Allylene-hydrogen bromide system

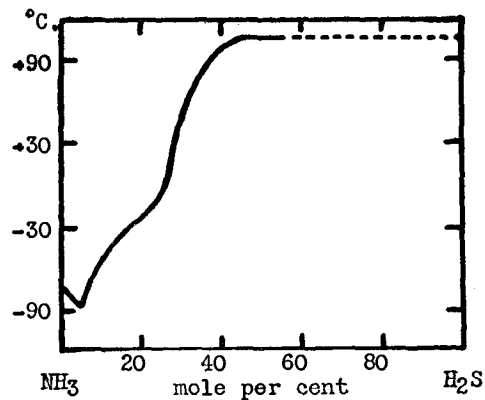


FIG. 6. Ammonia-hydrogen sulfide system

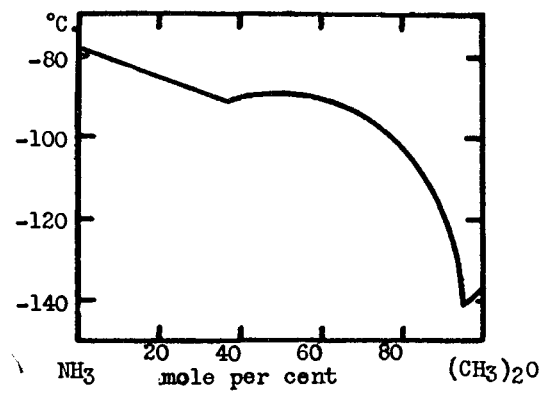


FIG. 7. Ammonia-methyl ether system

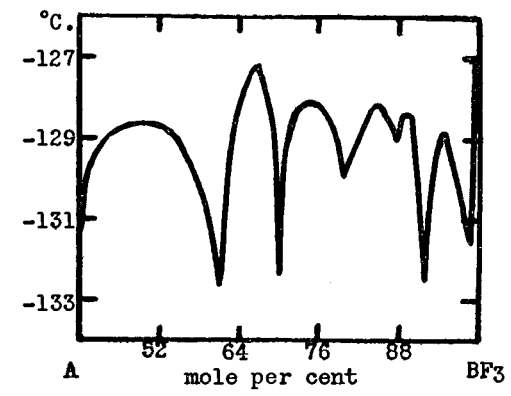


FIG. 8. Argon-boron trifluoride system

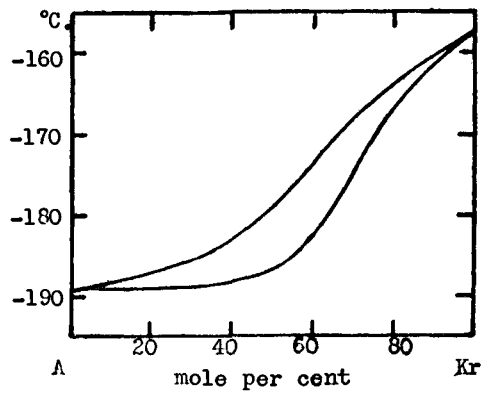


FIG. 9. Argon-krypton system

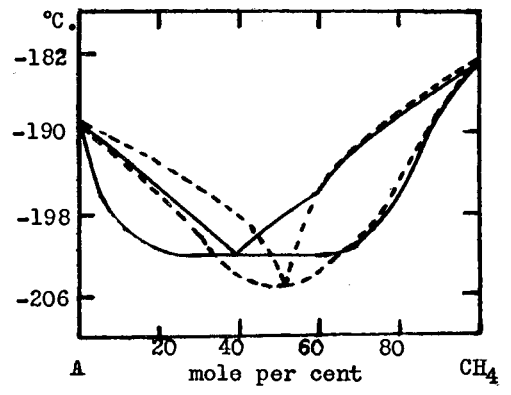


FIG. 10. Argon-methane system

8. Argon-methane (22, 44)

Argon, f.p. -189.0°C .; methane, f.p. -183.1°C . The point of equal concentrations lies around 60 mole per cent argon, and -201.9°C . (22). (See the solid-line curve in figure 10.)

Argon, f.p. approximately -189°C .; methane, f.p. approximately -182.4°C . Non-porous mixed crystals were formed with a point of equal concentrations at approximately 48 mole per cent argon and -205.4°C . (44). (See the broken-line curve in figure 10.)

9. Argon-nitrogen (22, 36)

Argon, f.p. -189.0°C .; nitrogen, f.p. -210.0°C . Solid solutions were formed (22). (See figure 11.)

10. Argon-oxygen (22, 36, 44)

Argon, f.p. -189.0°C .; oxygen, f.p. -219.0°C . Peritectic point occurred at about 20 mole per cent argon and -218.1°C . (22). (See the solid-line curve in figure 12.)

Ruhemann (36) reported this system as a degenerate peritectic type. The original reference was not available, so no data were obtained.

Argon, f.p. approximately -189°C .; oxygen, f.p. -218.9°C . A miscibility gap exists between 10 and 21 mole per cent argon with the peritectic point occurring at 10 mole per cent argon and -217.3°C . (44). (See the broken-line curve in figure 12.)

Veith and Schröder (44) reported that their data agreed with those of Ruhemann (36) fairly well on the argon side but that on the oxygen side there was a discrepancy in the vicinity of the peritectic point.

11. Boron trifluoride-hydrogen chloride (17)

Boron trifluoride, f.p. -127.0°C .; hydrogen chloride, f.p. -113.1°C . A eutectic occurred at 72.3 mole per cent boron trifluoride and -134.15°C . No compounds were reported. (See figure 13.)

12. Boron trifluoride-hydrogen sulfide (25)

Boron trifluoride, f.p. -128.5°C .; hydrogen sulfide, f.p. -82.0°C . Eutectics occurred at 78 mole per cent boron trifluoride and -147.5°C ., and at 53 mole per cent boron trifluoride and -137°C . The compounds $\text{BF}_3 \cdot \text{H}_2\text{S}$, f.p. -140°C ., and $\text{BF}_3 \cdot 7\text{H}_2\text{S}$, f.p. -99°C ., were found. (See figure 14.)

13. Boron trifluoride-methyl chloride (17, 20, 26)

Boron trifluoride, f.p. -118.5°C .; methyl chloride, f.p. -88.5°C . Maxima were reported for 33 mole per cent boron trifluoride and 15 mole per cent boron trifluoride. The suggestion was made that the methyl chloride was contaminated with methyl ether (26).

Boron trifluoride, f.p. -112°C .; methyl chloride, f.p. -78°C . This analysis was made with especially purified methyl chloride. A eutectic occurred at

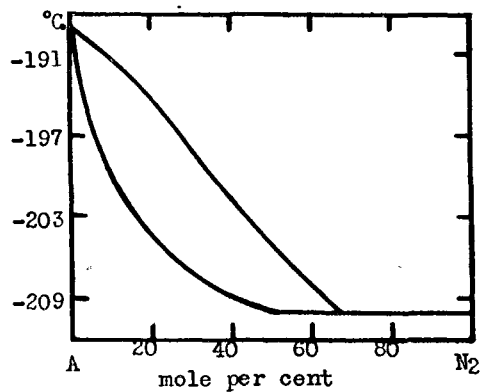


FIG. 11. Argon-nitrogen system

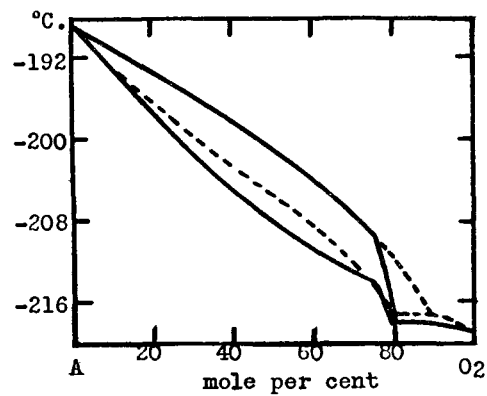


FIG. 12. Argon-oxygen system

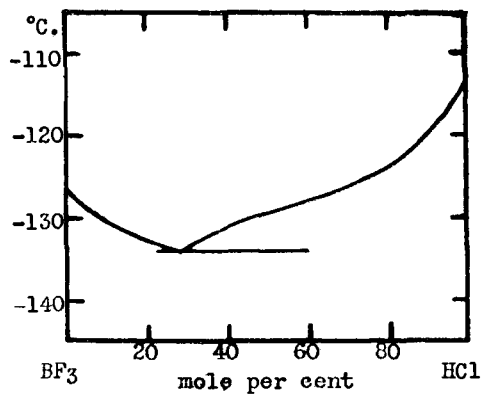


FIG. 13. Boron trifluoride-hydrogen chloride system

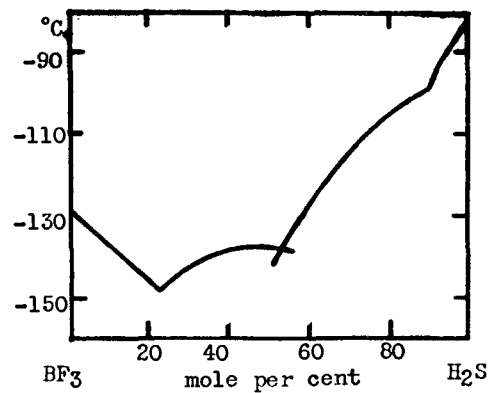


FIG. 14. Boron trifluoride-hydrogen sulfide system

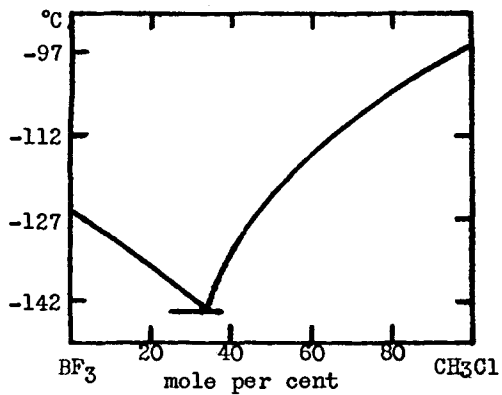


FIG. 15. Boron trifluoride-methyl chloride system

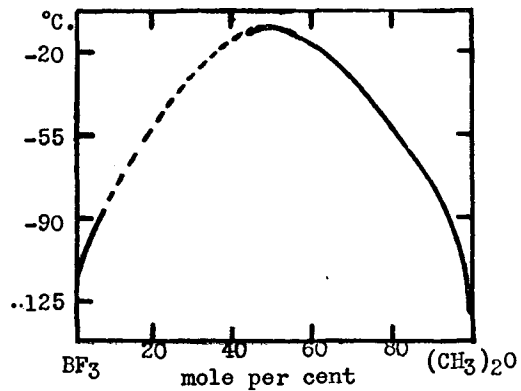


FIG. 16. Boron trifluoride-methyl ether system

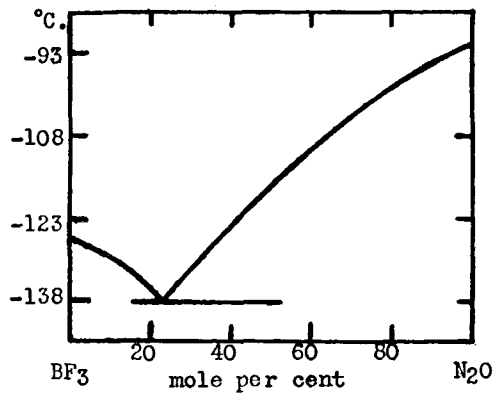


FIG. 17. Boron trifluoride-nitrous oxide system

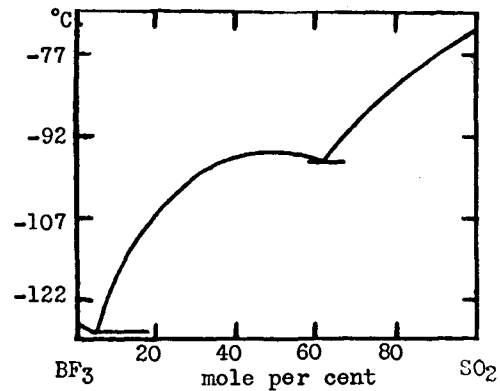


FIG. 18. Boron trifluoride-sulfur dioxide system

70 mole per cent boron trifluoride and -137°C . All temperatures were high, owing to the use of a pentane thermometer which was not corrected for stem emergence (20).

Boron trifluoride, f.p. -126.7°C .; methyl chloride, f.p. -96.65°C . A eutectic occurred at 65.5 mole per cent boron trifluoride and -144.8°C . No compounds were reported. (See figure 15 (17).)

14. Boron trifluoride-methyl ether (20, 26)

Boron trifluoride, f.p. -118.5°C .; methyl ether, f.p. -130.5°C . The compound $\text{BF}_3 \cdot (\text{CH}_3)_2\text{O}$, f.p. approximately -10°C ., was reported. The curve was incomplete, owing to excessive pressure on the boron trifluoride side, but it seemed to indicate a second compound between 60 and 90 mole per cent boron trifluoride. The temperatures were high, owing to the use of a propane thermometer without correction for stem emergence. (See figure 16.)

15. Boron trifluoride-nitrous oxide (17)

Boron trifluoride, f.p. -126.8°C .; nitrous oxide, f.p. -91.05°C . A eutectic occurred at 76.6 mole per cent boron trifluoride and -138.0°C . No compounds were reported. (See figure 17.)

16. Boron trifluoride-sulfur dioxide (17)

Boron trifluoride, f.p. -126.75°C .; sulfur dioxide, f.p. -73.5°C . Eutectics occurred at 38.0 mole per cent boron trifluoride and -97.15°C ., and at 95.2 mole per cent boron trifluoride and -128.6°C . The compound $\text{BF}_3 \cdot \text{SO}_2$, f.p. -96.0°C ., was found. (See figure 18.)

17. Butylene-hydrogen chloride (21)

β -Butylene, f.p. -127°C .; hydrogen chloride, f.p. -112°C . The diagram is incomplete with more than 67 mole per cent of β -butylene present.

The α -butylene-hydrogen chloride system was run only between 0 and 25 mole per cent α -butylene, because mixtures with more than 25 mole per cent α -butylene were liquids at liquid-air temperatures. (See figure 19.)

18. Carbon dioxide-methyl ether (12, 13)

Carbon dioxide, f.p. -56.7°C .; methyl ether, f.p. -137.6°C . A eutectic occurred at 22.5 mole per cent carbon dioxide and -144.8°C . No compounds were reported. (See figure 20.)

19. Carbon monoxide-nitrogen (29, 36, 38, 45)

Carbon monoxide, f.p. -204.9°C .; nitrogen, f.p. -210.0°C . No eutectic nor compound was found. A complete set of solid solutions was formed (29, 36, 38). (See the solid-line curve in figure 21.)

Carbon monoxide, f.p. -205.03°C .; nitrogen, f.p. -209.95°C . No eutectic nor compound was reported (45). (See the broken-line curve in figure 21.)

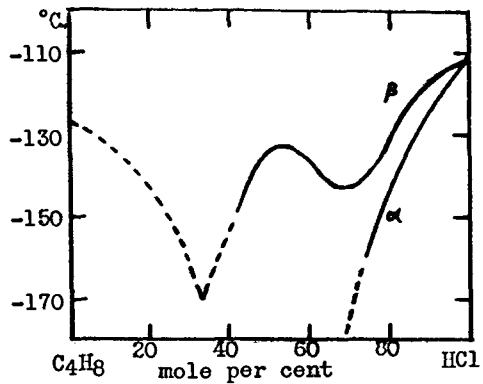


FIG. 19. Butylene-hydrogen chloride system

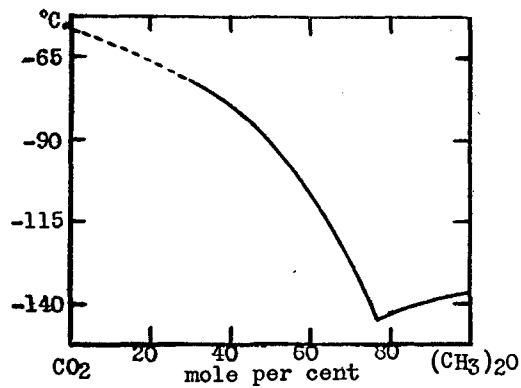


FIG. 20. Carbon dioxide-methyl ether system

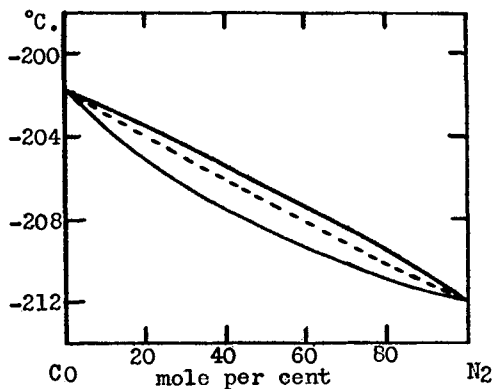


FIG. 21. Carbon monoxide-nitrogen system

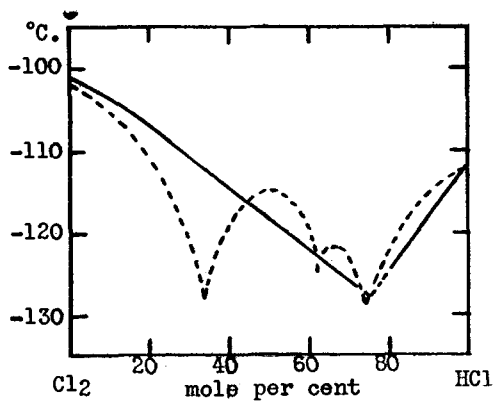


FIG. 22. Chlorine-hydrogen chloride system

20. Chlorine-hydrogen chloride (31, 47)

Chlorine, f.p. -101.5°C .; hydrogen chloride, f.p. -112.0°C . A eutectic occurred at 14.5 mole per cent chlorine and -127.5°C . No compound was reported. (See the solid-line curve in figure 22 (31).)

Chlorine, f.p. -102°C .; hydrogen chloride, f.p. -112°C . Eutectics were found at 26.3 mole per cent chlorine and -129°C ., at 38.0 mole per cent chlorine and -125°C ., and at 66.0 mole per cent chlorine and -128°C . The compounds $\text{Cl}_2 \cdot 2\text{HCl}$, f.p. -121°C ., and $\text{Cl}_2 \cdot \text{HCl}$, f.p. -115°C ., were reported. (See the broken-line curve in figure 22 (47).)

21. Chlorine-methyl chloride (46)

Chlorine, f.p. -102°C .; methyl chloride, f.p. -90°C . Eutectics occurred at 27.8 mole per cent chlorine and -124°C ., at 44.1 mole per cent chlorine and -120°C ., and at 63.3 mole per cent chlorine and -129°C . The compounds $\text{Cl}_2 \cdot 2\text{CH}_3\text{Cl}$, f.p. -120°C ., and $\text{Cl}_2 \cdot \text{CH}_3\text{Cl}$, f.p. -122°C ., were found. (See figure 23.)

22. Chlorine-nitrosyl chloride (19)

Chlorine, f.p. -94.4°C .; nitrosyl chloride, f.p. -64.5°C . A eutectic occurred at 57.5 mole per cent chlorine and -107.4°C . No compounds were reported. The freezing point given for chlorine is high, and the system should be reinvestigated. (See figure 24.)

23. Chlorine-sulfur dioxide (27, 41)

Chlorine, f.p. -100.9°C .; sulfur dioxide, f.p. -75.2°C . In the dark a eutectic was found at 97 mole per cent chlorine and -102.2°C . No compound was reported. In the light, eutectics were reported at 89 mole per cent chlorine and approximately -109.5°C . and at approximately 12 mole per cent chlorine and -84.5°C . (See figure 25.)

24. Ethane-hydrogen chloride (6, 7)

Ethane, f.p. -172.5°C .; hydrogen chloride, f.p. -111.6°C . Point of inflection is horizontally tangent at -125.2°C . No compound was reported. (See figure 26.)

25. Ethylene-hydrogen bromide (34)

Ethylene, f.p. approximately -167°C .; hydrogen bromide, f.p. -66.0°C . A eutectic occurred at approximately 85.4 mole per cent ethylene and -173.5°C ., and there was a slight depression at approximately 51 mole per cent ethylene and -161°C . No compound was found. (See figure 27.)

26. Ethylene-methane (36, 37)

Ethylene, f.p. -169.1°C .; methane, f.p. -182.6°C . A eutectic occurred at 12.2 mole per cent ethylene and -188.6°C . No compound was reported. (See figure 28.)

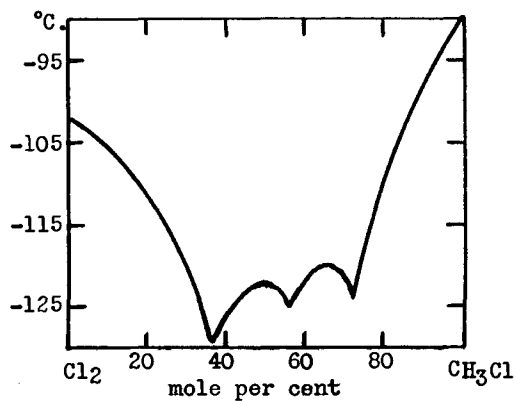


FIG. 23. Chlorine-methyl chloride system

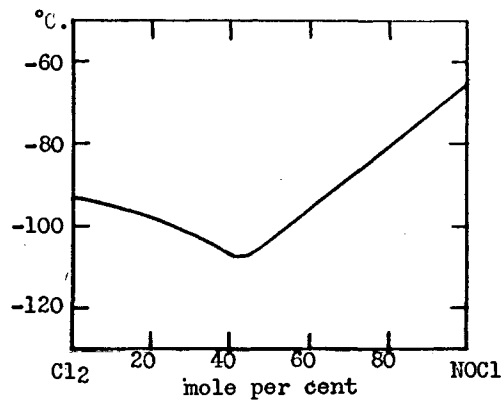


FIG. 24. Chlorine-nitrosyl chloride system

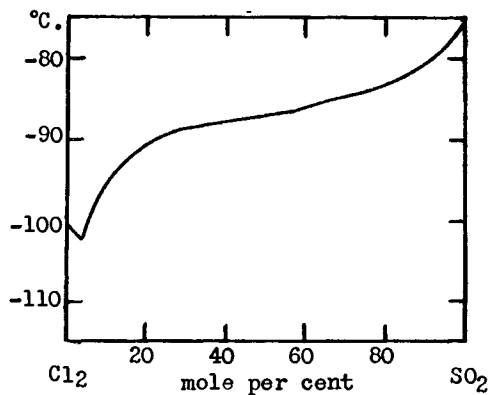


FIG. 25. Chlorine-sulfur dioxide system

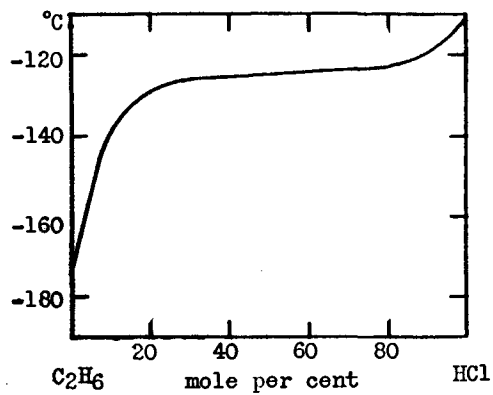


FIG. 26. Ethane-hydrogen chloride system

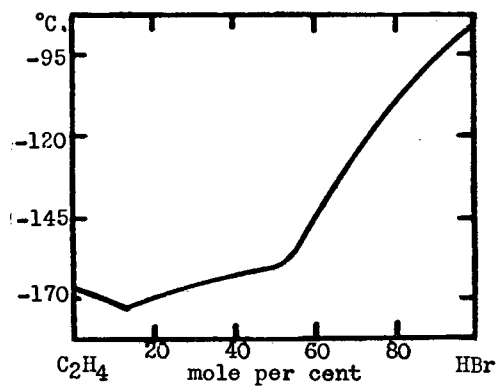


FIG. 27. Ethylene-hydrogen bromide system

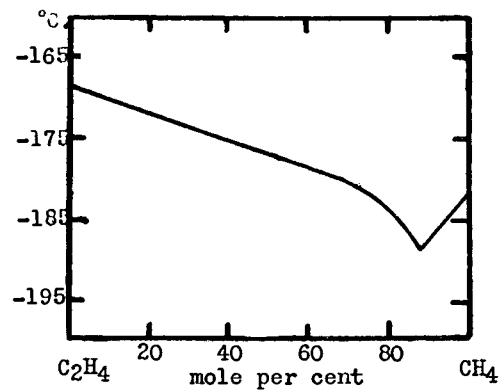


FIG. 28. Ethylene-methane system

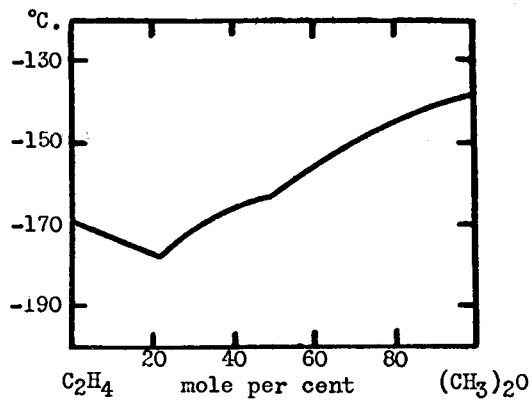


FIG. 29. Ethylene-methyl ether system

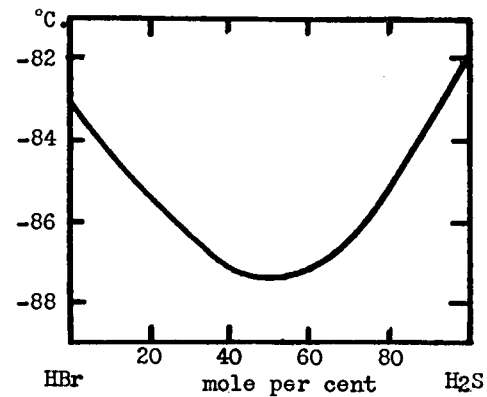


FIG. 30. Hydrogen bromide-hydrogen sulfide system

27. Ethylene-methyl ether (8)

Ethylene, f.p. $-169.5^{\circ}\text{C}.$; methyl ether, f.p. $-138^{\circ}\text{C}.$ A eutectic occurred at 79.5 mole per cent ethylene and $-178.5^{\circ}\text{C}.$ The unstable compound $\text{C}_2\text{H}_4 \cdot (\text{CH}_3)_2\text{O}$, f.p. $-163.2^{\circ}\text{C}.$, was found. (See figure 29.)

28. Hydrogen bromide-hydrogen sulfide (1)

Hydrogen bromide, f.p. $-83.0^{\circ}\text{C}.$; hydrogen sulfide, f.p. $-82.0^{\circ}\text{C}.$ A eutectic occurred at 49 mole per cent hydrogen bromide and $-87^{\circ}\text{C}.$ No compound was reported. (See figure 30.)

29. Hydrogen bromide-methyl ether (31)

Hydrogen bromide, f.p. $-86.0^{\circ}\text{C}.$; methyl ether, f.p. $-138.0^{\circ}\text{C}.$ A eutectic occurred at approximately 68 mole per cent hydrogen bromide and $-100^{\circ}\text{C}.$ The compound $\text{HBr} \cdot (\text{CH}_3)_2\text{O}$, f.p. $-13.0^{\circ}\text{C}.$, was found. The diagram is incomplete. (See figure 31.)

30. Hydrogen bromide-propylene (34)

Hydrogen bromide, f.p. $-86.0^{\circ}\text{C}.$; propylene, f.p. approximately $-185^{\circ}\text{C}.$ Eutectics occurred at approximately 26.7 mole per cent hydrogen bromide and $-196^{\circ}\text{C}.$, and at approximately 61.3 mole per cent hydrogen bromide and $-167.3^{\circ}\text{C}.$ The compound $\text{HBr} \cdot \text{C}_3\text{H}_6$, f.p. approximately $-166.6^{\circ}\text{C}.$, was found. (See figure 32.)

31. Hydrogen chloride-hydrogen sulfide (6, 7)

Hydrogen chloride, f.p. $-111.6^{\circ}\text{C}.$; hydrogen sulfide, f.p. $-82.6^{\circ}\text{C}.$ A eutectic occurred at approximately 72 mole per cent hydrogen chloride and $-117.5^{\circ}\text{C}.$ No compound was reported. (See figure 33.)

32. Hydrogen chloride-methyl chloride (5)

Hydrogen chloride, f.p. $-111^{\circ}\text{C}.$; methyl chloride, f.p. $-93.0^{\circ}\text{C}.$ A eutectic occurred at 72.7 mole per cent hydrogen chloride and $-161^{\circ}\text{C}.$ No compound was found. (See figure 34.)

33. Hydrogen chloride-methyl ether (2, 3, 4, 31)

Hydrogen chloride, f.p. $-111^{\circ}\text{C}.$; methyl ether, f.p. $-138.5^{\circ}\text{C}.$ The compounds $\text{HCl} \cdot (\text{CH}_3)_2\text{O}$, f.p. $-94^{\circ}\text{C}.$, and $4\text{HCl} \cdot (\text{CH}_3)_2\text{O}$, f.p. $-102^{\circ}\text{C}.$, were found (2).

Hydrogen chloride, f.p. $-111.3^{\circ}\text{C}.$; methyl ether, f.p. $-138^{\circ}\text{C}.$ Eutectics occurred at 7.5 mole per cent hydrogen chloride and $-147^{\circ}\text{C}.$, at approximately 62 mole per cent hydrogen chloride and $-123^{\circ}\text{C}.$, and at 91 mole per cent hydrogen chloride and $-122^{\circ}\text{C}.$ The compounds $\text{HCl} \cdot (\text{CH}_3)_2\text{O}$, f.p. $-97.1^{\circ}\text{C}.$, and $4\text{HCl} \cdot (\text{CH}_3)_2\text{O}$, f.p. $-103^{\circ}\text{C}.$, (4) and $-102.8^{\circ}\text{C}.$ (3), were found. (See the solid-line curve in figure 35.)

Hydrogen chloride, f.p. $-112.0^{\circ}\text{C}.$; methyl ether, f.p. $-138^{\circ}\text{C}.$ Eutectics occurred at 93.3 mole per cent hydrogen chloride and $-129^{\circ}\text{C}.$, and at 66.6 mole

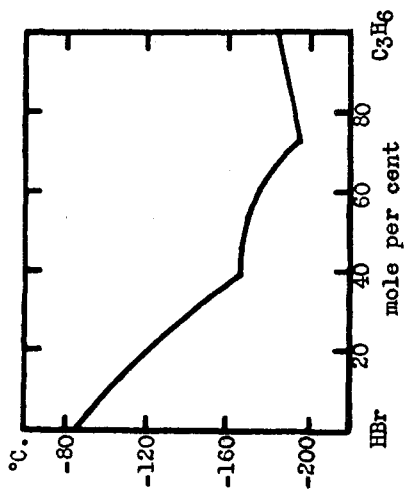


Fig. 32. Hydrogen bromide-propylene system

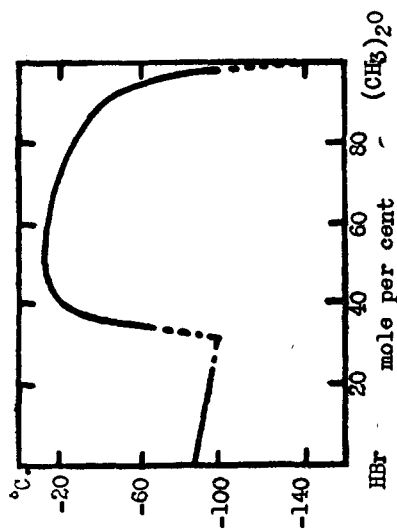


Fig. 31. Hydrogen bromide-methyl ether system

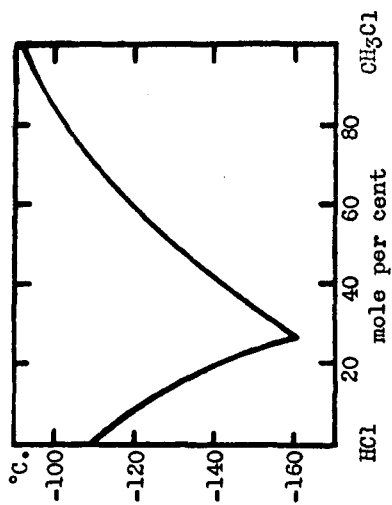


Fig. 34. Hydrogen chloride-methyl chloride system

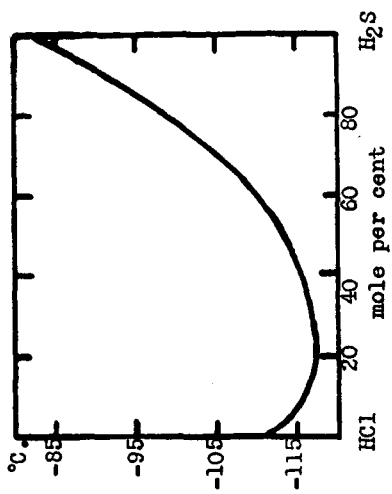


Fig. 33. Hydrogen chloride-hydrogen sulfide system

per cent hydrogen chloride and -121.2°C . The compounds $\text{HCl}\cdot(\text{CH}_3)_2\text{O}$, f.p. -96°C ., and 3 or 4 $\text{HCl}\cdot(\text{CH}_3)_2\text{O}$, f.p. -102°C ., were found (31). (See the broken-line curve in figure 35.)

34. Hydrogen chloride-nitric oxide (35)

Hydrogen chloride, f.p. -113°C .; nitric oxide, f.p. -153°C . The freezing points were located by the aid of conductivity measurements. The freezing points of mixtures the mole fractions of which approached 0.5 could not be determined, because the gases condensed as pure solid phases. A homogeneous liquid phase was obtained, with a pressure of 15 to 20 atmospheres, which had no conductivity, indicating the complex $\text{NOH}^+\cdot\text{Cl}^-$; this complex completely dissociated above -143°C . The freezing point given for nitric oxide is about 8°C . high.

35. Hydrogen chloride-sulfur dioxide (9, 10)

Hydrogen chloride, f.p. -112°C .; sulfur dioxide, f.p. -72°C . A eutectic occurred at 80 mole per cent hydrogen chloride and -133.5°C . No compound was reported. (See figure 36.)

36. Hydrogen iodide-hydrogen sulfide (1)

Hydrogen iodide, f.p. -46°C .; hydrogen sulfide, f.p. -82°C . A eutectic occurred at approximately 32 mole per cent hydrogen iodide and -90.8°C . No compound was found. (See figure 37.)

37. Hydrogen iodide-methyl ether (31)

Hydrogen iodide, f.p. -50.9°C .; methyl ether, f.p. not given. A eutectic occurred at 72.5 mole per cent hydrogen iodide and approximately -78°C . The compound $\text{HI}\cdot(\text{CH}_3)_2\text{O}$, f.p. -22°C ., was found. The diagram is incomplete. (See figure 38.)

38. Hydrogen sulfide-methyl ether (12, 13)

Hydrogen sulfide, f.p. -83.3°C .; methyl ether, f.p. -137.6°C . Eutectics occurred at 64.5 mole per cent hydrogen sulfide and -153.7°C ., and at 29.4 mole per cent hydrogen sulfide and -159.1°C . The compound $\text{H}_2\text{S}\cdot(\text{CH}_3)_2\text{O}$, f.p. -148.6°C ., was found. (See figure 39.)

39. Hydrogen sulfide-sulfur dioxide (15)

Hydrogen sulfide, f.p. approximately -83°C .; sulfur dioxide, f.p. approximately -72.5°C . A eutectic was found at 76 mole per cent hydrogen sulfide and -110°C . No compound was reported. (See figure 40.)

40. Krypton-methane (42, 44)

Krypton, f.p. -157.1°C .; methane, f.p. -182.6°C . A complete set of solid solutions consisting of non-porous mixed crystals was obtained (44). (See the solid-line curve in figure 41.)

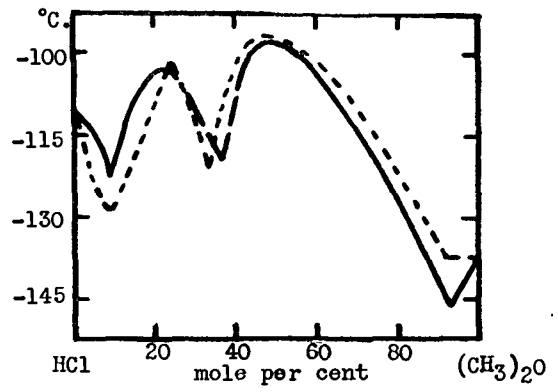


FIG. 35. Hydrogen chloride-methyl ether system

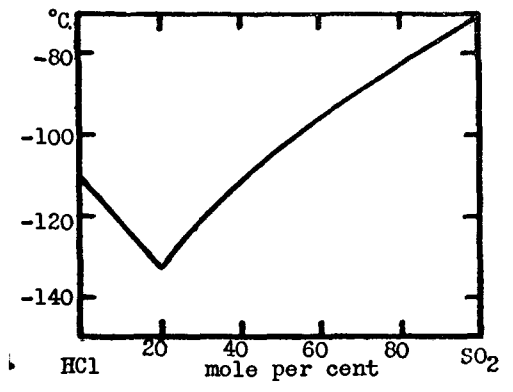


FIG. 36. Hydrogen chloride-sulfur dioxide system

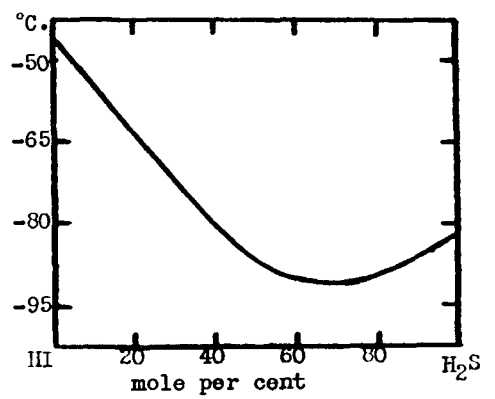


FIG. 37. Hydrogen iodide-hydrogen sulfide system

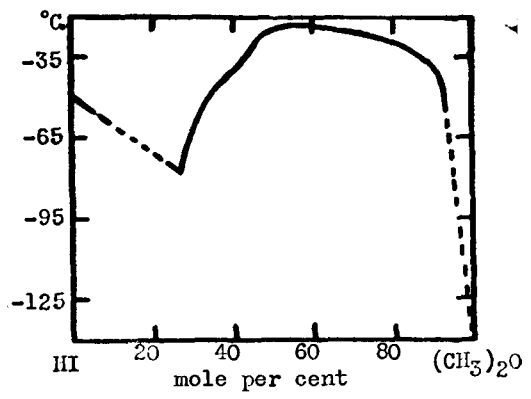


FIG. 38. Hydrogen iodide-methyl ether system

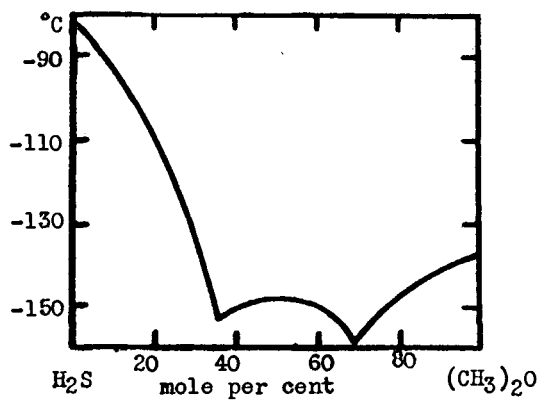


FIG. 39. Hydrogen sulfide-methyl ether system

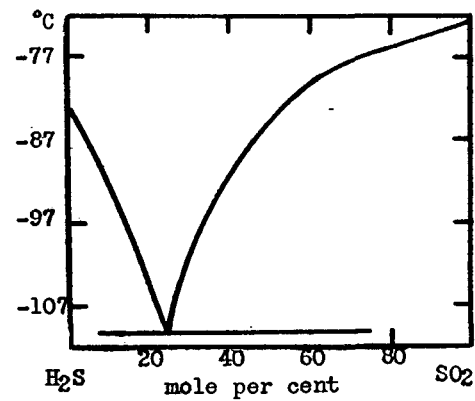


FIG. 40. Hydrogen sulfide-sulfur dioxide system

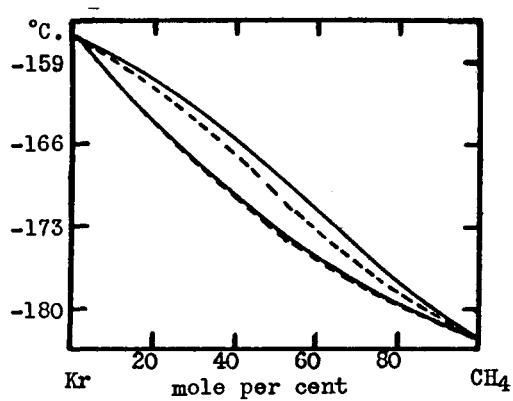


FIG. 41. Krypton-methane system

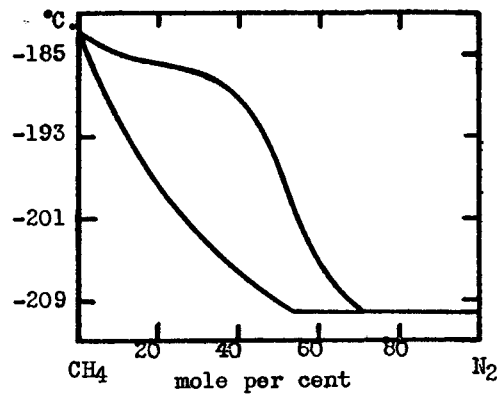


FIG. 42. Methane-nitrogen system

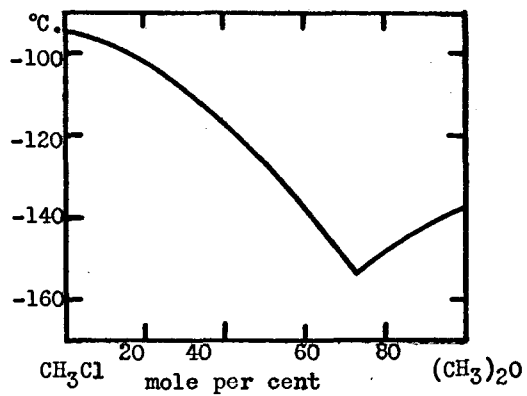


FIG. 43. Methyl chloride-methyl ether system

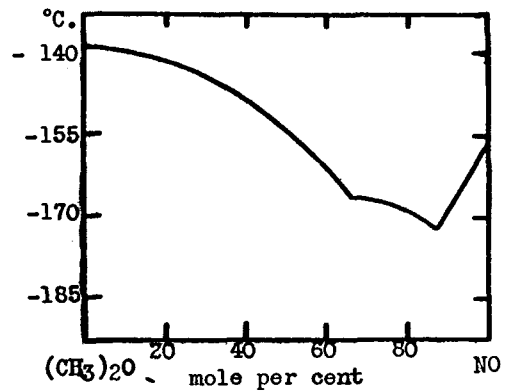


FIG. 44. Methyl ether-nitric oxide system

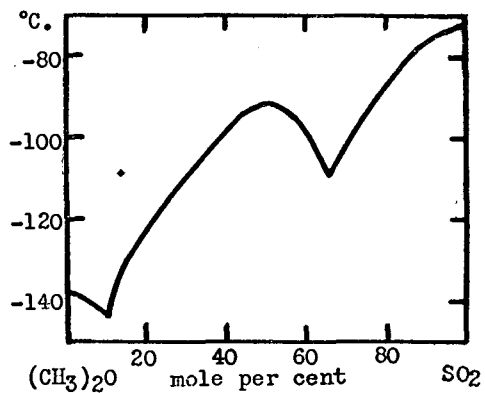


FIG. 45. Methyl ether-sulfur dioxide system

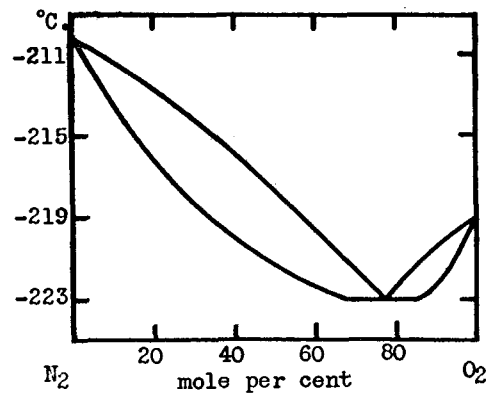


FIG. 46. Nitrogen-oxygen system

Krypton, f.p. $-157.1^{\circ}\text{C}.$; methane, f.p. $-182.6^{\circ}\text{C}.$ A complete set of solid solutions was obtained. The data are not in too good agreement with the above work (42). (See the broken-line curve in figure 41.)

41. Methane-nitrogen (22)

Methane, f.p. $-183.1^{\circ}\text{C}.$; nitrogen, f.p. $-210.0^{\circ}\text{C}.$ Peritectic point occurred around 30 mole per cent methane and $-210.0^{\circ}\text{C}.$ (See figure 42.)

42. Methyl chloride-methyl ether (2, 4)

Methyl chloride, f.p. $-94.5^{\circ}\text{C}.$; methyl ether, f.p. $-138.5^{\circ}\text{C}.$ A eutectic occurred at 27 mole per cent methyl chloride and $-154^{\circ}\text{C}.$ No compound was reported. (See figure 43.)

43. Methyl ether-nitric oxide (8)

Methyl ether, f.p. $-138^{\circ}\text{C}.$; nitric oxide, f.p. $-161^{\circ}\text{C}.$ A eutectic occurred at 12.5 mole per cent methyl ether and $-172^{\circ}\text{C}.$ The compound $(\text{CH}_3)_2\text{O}\cdot 2\text{NO}$, f.p. $-166.3^{\circ}\text{C}.$, was found. (See figure 44.)

44. Methyl ether-sulfur dioxide (2, 4)

Methyl ether, f.p. $-138.0^{\circ}\text{C}.$; sulfur dioxide, f.p. $-72.3^{\circ}\text{C}.$ Eutectics occurred at 34 mole per cent methyl ether and $-109^{\circ}\text{C}.$, and at 88.5 mole per cent methyl ether and $-144^{\circ}\text{C}.$ The compound $(\text{CH}_3)_2\text{O}\cdot\text{SO}_2$, f.p. $-91.5^{\circ}\text{C}.$, was found. (See figure 45.)

45. Nitrogen-oxygen (29, 36, 38)

Nitrogen, f.p. $-210.0^{\circ}\text{C}.$; oxygen, f.p. $-219.0^{\circ}\text{C}.$ A eutectic occurred at 22.5 mole per cent nitrogen and $-223.0^{\circ}\text{C}.$ No compound was reported. (See figure 46.)

VII. SUMMARY

A critical survey of the field of thermal analysis of liquefied gases has been made. The field was limited to binary systems in which both components were gases under standard conditions.

The methods used to establish mole fractions and to determine their freezing points were reviewed, and the procedure used at this laboratory was analyzed for possible sources of error.

Forty-five binary systems were found in the literature and the salient facts about each system presented. The phase-rule diagrams for forty-four of these systems were included. Errors in some of the work are obvious and some of these systems should be reinvestigated. These errors were probably due to impurities in the components, or to inferior methods for temperature measurements.

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