The Ternary System Carbon Monoxide-Nitrogen-Hydrogen and the Component Binary Systems between Temperatures of - 185 degrees and - 215 degrees C., and between Pressures of 0 and 225 Atm.

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Phil. Trans. R. Soc. Lond. A 1932 **230**, 189-220
doi: 10.1098/rsta.1932.0006

VI. *The Ternary System Carbon Monoxide–Nitrogen–Hydrogen and The Component Binary Systems between Temperatures of* − 185° *and* − 215° *C., and between Pressures of* 0 *and* 225 *Atm.*

By T. T. H. Verschoyle.

(*Communicated by* F. A. Freeth, *F.R.S.*)

(Received April 28, 1930—Read January 22, 1931.)

I.—Experimental Apparatus and Methods.

§ 1. *Introduction.*

The investigation of two- and three-phase equilibria at low temperatures and high pressures appears hitherto to have been limited almost exclusively to single-component systems. A very few researches on binary systems at low temperatures, such as those of Holst and Hamberger* on argon and nitrogen, and of Kuenen and Clark†, of Kuenen, Verschoyle and van Urk‡, and of Barnett, Dodge and Dunbar§ on oxygen and nitrogen have been published. No other work on binary systems at low temperatures and high pressures can be traced, and the field of ternary systems at low temperatures would seem to be entirely unexplored.

The present researches concern a ternary system which is of importance in the consideration of the technical production of hydrogen by low temperature methods. Both the ternary system itself and the two binary systems, carbon monoxide-hydrogen and nitrogen-hydrogen, were investigated under conditions where the temperature lies well above the critical temperature of one component, but well below that of the other component (or components).

The designs of the requisite cryogenic installation were based almost entirely on the apparatus and methods in use at the Physical Laboratory of the Leiden University. A detailed description of the apparatus is therefore unnecessary, but, inasmuch as the whole investigation is somewhat long and involved, it has been thought advisable to divide this account into two parts, the first of which deals with the experimental apparatus and methods.

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* ‘Z. Physikal. Chem.,’ vol. 91, p. 513 (1916).
† ‘Phys. Lab. Leiden, Commn.’ No. 150*b*.
‡ ‘Phys. Lab. Leiden, Commn.’ No. 161.
§ ‘J. Amer. Chem. Soc.,’ vol. 49, p. 591 (1927).

[Published July 14, 1931.

§ 2. *Apparatus.*

(*a*) *Mixing Apparatus, Volumenometer and Piezometer.*—The design and use of these pieces of apparatus have already been described.* It should be noted that, with the exception of a single set of determinations, the piezometer was not used during this research for the measurement of volumes, but either as a reservoir for the storage of the necessary quantities of gas under pressures of a few atmospheres, or for determining the difference in pressure between that shown by the pressure-balance, and the effective pressure to which the system was exposed.

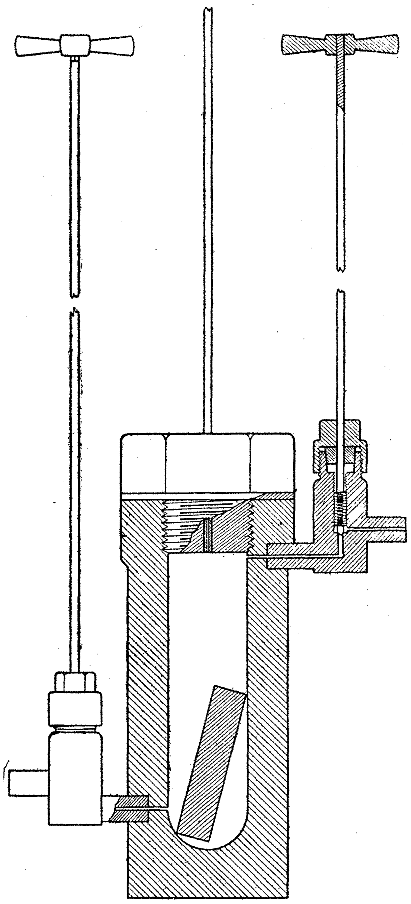
FIG. 1.—Complex Equilibrium-Vessel. (Scale 1 : 1·5).

(*b*) *Equilibrium-Vessel.*—Two forms of equilibrium-vessel were used. One, the " Simple " form, consists of a brass cylinder of about 1 cm.^{3} capacity, containing a small iron rod (to act as a stirrer) and connected by means of a nut and collar to the steel capillary which leads to the piezometer.

The second type of equilibrium-vessel, the "Complex" form, is illustrated in fig. 1. The purpose of this vessel was to allow of the drawing off of samples of the vapour and liquid phases after equilibrium had been attained. It consists of a brass cylinder of about 9 cm.^{3} capacity containing a stirrer, and it is fitted with small high-pressure taps, the spindles of these taps being long enough to extend through the cover of the cryostat. It was a matter of some difficulty to find a suitable material for the glands of the taps, which were exposed to liquid-air temperatures. Eventually, with the aid of well-dried discs of cork, it was found possible to make them tight against a vacuum, after long usage.

(*c*) *Thermostat.*—When it was necessary to effect any determinations of volume at normal temperature the thermostat previously described was used.

(*d*) *Cryostat.*—The cryostat, which is illustrated in fig. 2, is of the usual Leiden pattern. It consists essentially of a vacuum-glass to contain the necessary liquid oxygen, closed by a vacuum-tight cap of German silver. To the cap are fitted guides, through which pass the steel capillary leading to the equilibrium-vessel (*r*); the leads to the two resistance thermometers (one only is shown, T); a hydrogen thermometer (H), when required; the support for a pump stirrer (P) and the mechanism actuating it; an inlet (A) and an outlet (B) for the liquid oxygen of the cryostat; and a wide connection leading to the vacuum pumps. When the complex equilibrium-vessel is used, guides

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* 'Proc. Roy. Soc.,' A, vol. 111, p. 552 (1926).

are also required for the spindles of the two taps as well as for the support of the vessel, so that the cap area is somewhat congested.

The stirring of the contents of the equilibrium-vessel is effected through the agency of a soft iron sheath (S), a large ring-magnet and an automatic make-and-break. The pump-stirrer in the liquid oxygen is actuated, as shown, by means of a horseshoe-magnet moving through a short vertical interval.

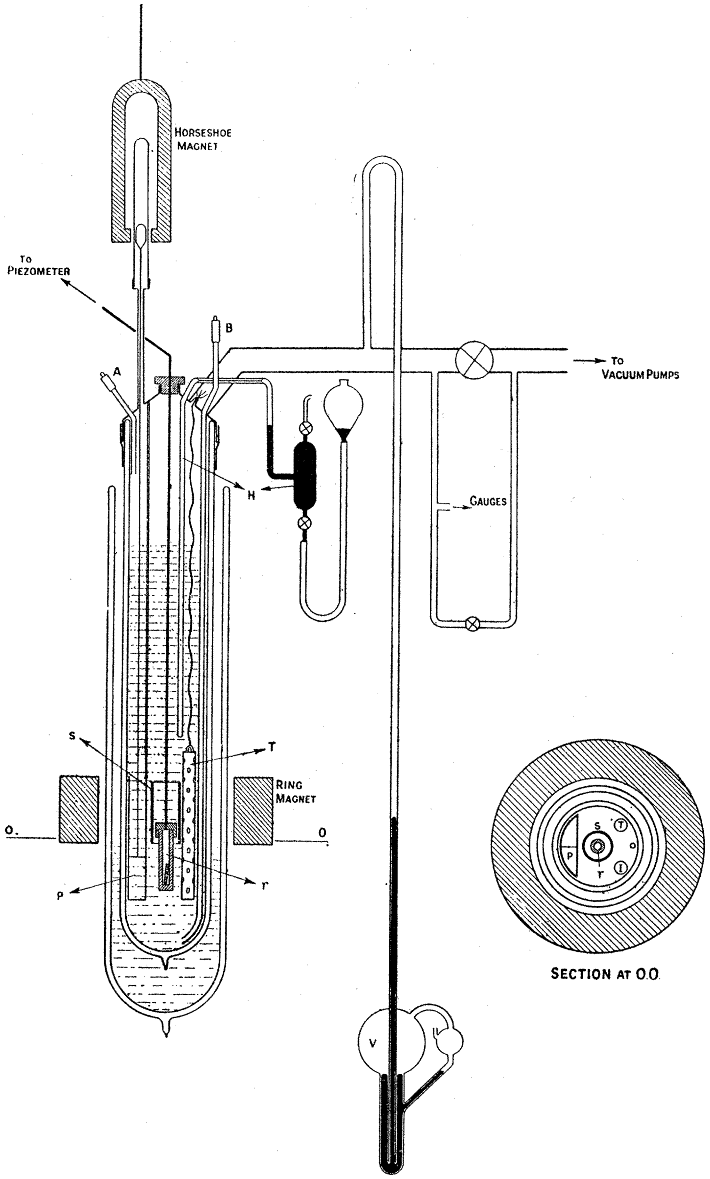

Fig. 2.—Cryostat. (Scale 1 : 8).

The cryostat is placed within a second vacuum-glass containing liquid air. Both glasses are silvered, clear strips being left for observational purposes.

(*e*) *Oxygen-circuit.*—As already mentioned, the cryostat cap is fitted with a vacuum connection; this is a 1-in. copper pipe which leads, through a valve, to a 3-in. pipe connected to the vacuum pumps. A safety-tube (V, fig. 2), and a by-pass and gauges are fitted, the fine regulation of the pressure within the cryostat (and thus of the temperature) being effected with the help of a differential oil-gauge.

The two vacuum-pumps are by Burckhardt, with capacities of 20 and 120 $M.^3$/hr. respectively, and are so arranged that either can run singly, or both run in series : in the latter case, it is possible to reduce the pressure in the cryostat to about 1 mm. From the compression-side of the vacuum-pumps a pipe leads to a gas holder of 1 $M.^3$ capacity, with a side branch leading to a small oxygen compressor ; when necessary, the cryostat may be put into direct communication with the gas-holder.

(*f*) *Manometers.*—Pressures up to two atmospheres were read on a syphon manometer of a design slightly modified from that described by Holborn and Henning.*

For pressures up to 225 atmospheres, the pressure-balance previously described was used.

(*g*) *Thermometers.*—Normal temperatures were read on thermometers graduated in tenths of a degree ($1° \equiv 1$ cm.), which had been checked against a standard thermometer.

Low temperatures were measured with the aid of two platinum resistance thermometers, which the Physical Laboratory at Leiden very kindly supplied. These thermometers were compared with the Leiden standard resistance thermometers, and were subsequently checked against the accurately known vapour pressures of oxygen. The freezing-point resistances were also frequently determined, and found to remain satisfactorily constant.

Resistances were measured by Kohlrausch's method of overlapping shunts,† whereby all lead irregularities are eliminated.

(*h*) *Analysis Apparatus.*—Samples of the vapour and liquid phases in the complex equilibrium-vessel were pumped off through the respective taps, collected in gas pipettes, transferred to a Bone and Wheeler gas-analysis apparatus, and analysed by explosion and absorption.

§ 3. *Preparation of Gases.*

Hydrogen and nitrogen were prepared as previously described. Carbon monoxide was prepared by the action of sulphuric acid on anhydrous sodium formate. A mixture of about 200 $cm.^3$ of sulphuric acid and 40 $cm.^3$ of water was heated *in vacuo* until violent bumping occurred. The vessel containing the acid mixture was allowed to cool, and then it was rotated about a ground joint, in such a way that the mixture flowed into another vessel containg 35 grams of sodium formate and cooled in a freezing mixture. The evolution of carbon monoxide was readily controlled by regulating the

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* 'Ann. Physik,' vol. 26, p. 833 (1915).

† 'Lehrbuch Prakt. Physik,' 13th ed., p. 427.

supply of heat to the reaction vessel, and the gas, after passing through a trap and spiral immersed in liquid air, was condensed in a glass tube cooled by liquid air boiling under reduced pressure. It was then allowed to evaporate, the head and tail fractions of the condensate being rejected, and the remainder collected in a small (1 L.) gas cylinder. A satisfactory test of the purity of the carbon monoxide was afforded by determinations of the vapour pressure (given in detail later).

§ 4. *Experimental Methods.*

Part I of this paper may suitably be brought to a close with a brief account of the distinct experimental operations involved in this research :—

(*a*) *Vapour Pressures up to 2 atms.*—For the determination of the vapour pressures of carbon monoxide between — 185° and — 215° C. (the only vapour pressures required for this research, those of nitrogen being already known), a static method was employed. The syphon manometer was connected to a glass tube, about 8 mm. in diameter, ending in a small bulb, which was fitted in the cryostat, and branch connections led to a supply of carbon monoxide and to a vacuum pump. The glass tube was enclosed in one of brass, slit along its whole length for observational purposes, to ensure that the temperature of the former was not lower than that of the bulb. The positions of the mercury menisci in the manometer and, when necessary (for the higher pressures) in a syphon barometer, were read with a cathetometer, by the Société Genevoise, reading to 0·02 mm. Manometer, barometer and cathetometer were all mounted on a heavy slate slab supported on a large concrete table and foundation.

(*b*) *Liquid-vapour Equilibria* (*Volumetric Method*).—Before the analytical method of investigating liquid-vapour equilibria was devised, one series of determinations was carried out (with the system carbon monoxide-hydrogen) by a volumetric method. This method was based on the measurement of the segments of $p - v_A$ isotherms in the neighbourhood of the border curve, for mixtures of definite compositions. Unfortunately, with two gases differing widely in their critical constants, the break in the isotherm is not very marked and, moreover, its approximate position was entirely unknown. Consequently, an extremely large number of points (almost 500) had to be measured for the derivation of only two $p - x$ isotherms, and each of these points involved a laborious computation, comprising some 40 separate calculations. The results are, however, of value as confirming completely those obtained by the entirely different method subsequently developed.

The simultaneous measurements of pressure (on the pressure-balance), of temperature (of the cryostat, the piezometer stem, and the steel capillary), and of volume (as given by the resistance of the platinum wire in the piezometer stem) are straightforward, and require no description. All observations are made with rising pressure, and before measurements are made at a new temperature, the pressure must be entirely released, and, if necessary, the temperature of the cryostat allowed to rise, to ensure that no condensed liquid remains in the equilibrium vessel.

(*c*) *Liquid-vapour Equilibria* (*Analytical Method*).—It became evident very soon that some method differing radically from that just described would have to be devised, if any real progress at all was to be made with the research. The chief obstacle to progress was the laborious volume determination, and it was decided, therefore, to limit the investigation to the direct measurement of pressure, temperature, and composition of the co-existing phases (by analysis). The principle is simple enough, but the exposure of the necessary sampling taps to pressures of 200 atmospheres at temperatures of —200° C. occasions certain difficulties.

The general assembly of the apparatus will be clear from fig. 3. About 30 L. of the mixed gases were prepared and compressed into the gas cylinder C of 1 L. capacity, from which the mixture passed through a copper spiral S, immersed in a mixture of solid carbon dioxide and alcohol (to remove any traces of moisture), and through the small steel tap 1 into the measuring system. The portion of the apparatus included between the tap 1 and the coupling X comprised the piezometer, steel capillary and connections to the pressure balance, as previously described.

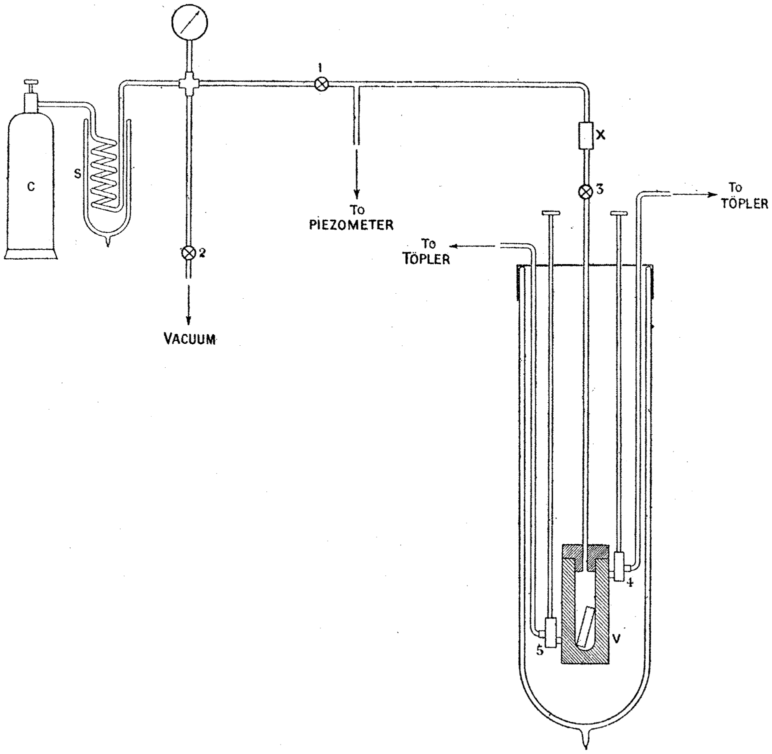

FIG. 3.—Scheme of Apparatus.

In order to effect a series of determinations, the whole train of apparatus up to the sampling taps (except the cylinder C) is evacuated through tap 2. The requisite quantity of gas* is admitted into the piezometer and equilibrium-vessel through tap 1, and the latter closed. The stirrer is kept at work in the equilibrium-vessel, and, when the desired temperature and pressure equilibria have been attained, tap 3 is closed and the stirrer stopped. Samples of about 25 cm.^{3} of gas are then simultaneously extracted through taps 4 and 5, these samples blowing straight into the two Töpler pumps. Reference to some necessary precautions will be made in § 5.

When working in the neighbourhood of the plait-point, it is essential that the composition of the mixture used should be approximately that of the plait-point mixture; otherwise only one phase may be present. The proper mixture can be attained only by trial and error, and determinations effected close to the plait-point are inevitably somewhat tedious.

(*d*) *Liquid-vapour Equilibria* (*at Low Pressures*).—A few determinations were carried out with the system carbon monoxide-nitrogen, the observational tube of § 4 (*a*) being replaced by a glass capillary tube about 50 cm. long and ½ mm. bore, terminating in a cylindrical bulb which was of some 800 mm.^{3} capacity and contained an electromagnetic stirrer. The apparatus could be filled with a mixture of known composition.

The method of investigation consisted in noting the pressure at which, at a given temperature, the first drop of liquid could be seen in the observational tube, and the pressure at which the last bubble of vapour condensed. The latter pressure is far the easier of the two to observe, and, indeed, it was found that the observations of the former were almost worthless, largely because the liquid-vapour " lens " is in this case very narrow.

(*e*) *Melting-point Curves.*—In the case of carbon monoxide and nitrogen, the relation between the pressure and the temperature of the melting-point was investigated by a very simple method. The gas was condensed in the simple equilibrium-vessel, and the pressure raised to the desired value. The temperature, which had been maintained above the melting-point, was then allowed to drop until the movement of the stirrer could no longer be heard, indicating that the contents of the reservoir were frozen.

When the cryostat was now allowed to warm up slowly, it was found that, following on a slow rise, the resistance of the stem wire suddenly began to increase very rapidly, indicating that gas was evaporating back into the piezometer. This showed that the steel capillary, which had hitherto been blocked by a plug of the solid phase, was now free, and hence that the melting-point had been reached. In practice, the temperature was allowed to rise fairly quickly until within about a quarter of degree of the assumed melting-point, and the rate was then checked to 0·03–0·05° per minute. At this rate, the galvanometer reading remained practically constant until, at the melting-point, it moved up quite suddenly.

This method is thus based on the melting of a very small plug in the steel capillary (of ½ mm. bore), and it appears to lead to very accurate results, as will be seen subsequently.

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[*] At the desired temperature and pressure, the mercury must stand in the piezometer stem.

In the case of the system carbon monoxide-nitrogen, the freezing-point curve was determined by visual observation. It was not possible, with the apparatus used, to determine the melting-point curve with any accuracy, although it was obvious that it lay very close to the freezing-point curve.

(*f*) *Solid-vapour Equilibria.*—It was found possible to determine the vapour branches of the $p - x$ isotherms with the apparatus used for liquid-vapour equilibria; the solid phase was, of course, inaccessible. Briefly, the method consisted in commencing with a liquid-vapour equilibrium at about the triple-point temperature, stopping the stirrer, and lowering the temperature to the required point, while simultaneously slowly increasing the pressure to the highest employed. In this way, it was generally possible to keep the capillary open, although it frequently froze up while an observation was being made. Successive determinations were always made with dropping pressures, to ensure that equilibrium was approached with a vapour supersaturated as regards the solid phase.

(*g*) *Triple-points.*—The pressure and temperature of the triple-points were determined by the method described in § 4 (*a*).

(*h*) *Three-phase Curves.*—The course of the three-phase curves (the projection of the three-phase strip on the $p - t$-plane) was investigated by an auditory method, in the case of the two binary systems carbon monoxide-hydrogen and nitrogen-hydrogen After a liquid-vapour equilibrium had been established in the equilibrium-vessel at the desired pressure, the electromagnetic stirrer was stopped. The temperature was allowed to fall and the mobility of the stirrer frequently tested, until it became apparent to the ear that the stirrer was frozen in the solid phase. The magnet controlling the stirrer was then switched on, and the temperature was allowed to rise slowly (at an approximate rate of 0·05° per minute) until the stirrer was heard to move again. The reading of the temperature taken at this moment was assumed to be the temperature corresponding to the given pressure on the three-phase line.

In the case of the binary system carbon monoxide-nitrogen, the three-phase line was derived from visual observation of the melting of minute crystals.

§ 5. *Sources of Errors.*

Before proceeding to a consideration of the experimental results, the probable sources and magnitudes of error will be discussed.

In determinations of low pressures (below 2 atmospheres) the cathetometric error is not greater than ±0·002 cm. High pressures, as determined by the pressure balance, are given to the nearest tenth of an atmosphere, although, at pressures over 20 atmospheres the error probably does not exceed ±0·05 atmosphere; at pressures less than 20 atmospheres the balance tends to become less sensitive.

As already stated, the platinum resistance thermometers were found to remain extremely constant. Originally compared with the standard resistance thermometers at Leiden, and subsequently checked against the known vapour pressures of oxygen, their accuracy is such that it is improbable that errors in temperature observations exceeded ±0·02° C.

The largest errors are associated with the composition of the various phases, except in the few investigations concerned with mixtures made up in known proportions. The analytical determinations of composition may be affected by several sources of error. In the first place, the removal of two volumes of about 25 cm.^{3} of gas (at N.T.P.) from the equilibrium-vessel involves a reduction in pressure of approximately 5 per cent. and 1 per cent. at the lowest and highest pressures respectively. The effect of this reduction would be of little consequence if the samples were taken rapidly, simultaneously, and of the correct volume. Unfortunately, owing to the necessary tightness of the glands on the sampling taps, it was rarely possible to satisfy these conditions, although the technique improved with practice. Nevertheless, the consequent error becomes serious only near the plait-point, where $\partial x/\partial p$ assumes a large value.

A second source of error, which applies only to the vapour sample, arises from the mixing of the gas contained in the capillary below tap 3 (fig. 3) with the vapour phase, consequent on the pressure reduction. The volume of this space, however, is only 100 mm.^{3}, so that at the lowest pressures (for which the composition of the gas in the capillary and in the vapour phase differ most) not more than 1 per cent. could mix with the vapour sample.

Thirdly, there is a dead space of 2–3 mm.^{3} between the spindles of the sampling taps and the central space of the equilibrium-vessel. Near the plait-point, the volume of gas (at N.T.P.) contained in this space might amount to 1–2 cm.^{3}, or perhaps 8 per cent. of the sample. Unless, therefore, these dead spaces be "washed out" with the liquid and vapour phases respectively before sampling, an error will arise, affecting principally the liquid phase. In some of the earlier determinations the existence of this error was not taken into account.

Failure to wash out the dead spaces before sampling was responsible also for a fourth possible error during the investigation of the system carbon monoxide-hydrogen. This arises from the splashing of a droplet of the liquid phase into the canal leading to the vapour tap, and, since at low pressures the liquid consists almost entirely of carbon monoxide, $\frac{1}{2}$ mm.^{3} of liquid included in the vapour sample would lead to a positive error of one in the percentage of carbon monoxide.

Owing to the difficulty of making the glands on the sampling taps vacuum-tight during the earlier series of investigations on the system carbon monoxide-hydrogen, leakages of oxygen from the bath into the samples frequently occurred. The percentages of carbon monoxide and hydrogen found were therefore increased in the same proportion to make the total 100. By the time the investigation of the system nitrogen-hydrogen commenced, this difficulty had been overcome.*

A final source of error was not realised until the close of the researches on the binary

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* Several months of repeated slight adjustments were necessary.

systems. Up till then, the vapour samples had been collected under approximately atmospheric pressure, but it became apparent then that these also, like the liquid samples, should be pumped off. The reason for this lies in the fact that, at the lowest temperatures and highest pressures the partial pressure of the carbon monoxide (or nitrogen) in the vapour samples approximates to the vapour pressure of carbon monoxide (or nitrogen). The cooling effect produced by blowing off the sample will therefore suffice to deposit solid carbon monoxide (or nitrogen) in the capillary, from which it will but slowly evaporate.

II.—Experimental Data and Discussion of Results.

§ 6. *One-Component Systems.*

(*a*) *Carbon Monoxide.*—Vapour pressures and melting-point curve.

Observations on the vapour pressures of carbon monoxide have been made by Olszewski* (mainly of historical interest); by Baly and Donnan,† between —185° and —205° C.; and by Estreicher and Bobotek,‡ between —188° and —208° C. The agreement between the published results is not good, and it was therefore thought advisable to carry out a new determination of the vapour pressures between —185° and —218° C., and also to measure the triple-point; the results are reproduced in Table I, in which the data for each point represent the mean of two concordant observations. One set of measurements was made with the observational bulb almost empty, and another with it almost full; it will be seen that the agreement between the two sets of results is very satisfactory:—

Table I.—Carbon Monoxide—Vapour Pressures.

Bulb " empty " (E) or " full " (F).	Pressure cm.	Observed temperature.	Calculated temperature.
		°	°
E	143·15	—185·44	—185·43
F	·14	·44	
E	110·10	—188·06	—188·05
F	·08	·06	
E	81·27	—190·87	—190·86
F	·36	·86	

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* 'C. R.,' vol. 99, p. 706.

† 'J. Chem. Soc.,' p. 902 (1902).

‡ 'Anzeiger Akad. Wiss. Krak.,' vol. 7, p. 461 (1913).

TABLE I—(continued).

Bulb "empty" (E) or "full" (F).	Pressure. cm.	Observed temperature.	Calculated temperature.
		°	°
E	70·86	—192·07	—192·07
F	·94	·07	
E	56·66	—193·95	—193·95
F	·54	·96	·97
E	40·79	—196·55	—196·54
F	·76	·55	
E	27·89	—199·33	—199·32
F	·94	·32	·31
E	18·005	—202·27	—202·25
F	·013	·27	
F	11·605	—204·96	—204·96
F	11·495	—205·01	—205·01
F (T.P.)	11·486	—205·03	—205·00
E	7·045	—207·43	—207·44
F	·040	·43	
E	3·294	—210·82	—210·80
F	·297	·81	
F	·304	·81	·79
E	1·987	—212·78	—212·81
F	·975	·79	·83
E	0·886	—215·71	—215·70
F	·890	·69	·68
E	0·326	—218·88	—218·85
F	·325	·87	

The vapour pressures of liquid CO and of solid CO may be represented by the following equations :—

$$\left.\begin{aligned}\text{Log}\ p &= -\frac{691\cdot91}{\text{T}} + 6\cdot9059 - 0\cdot006044 \times \text{T}\\[2em] \text{Log}\ p &= -\frac{520\cdot85}{\text{T}} + 10\cdot7005 - 0\cdot02923 \times \text{T}\end{aligned}\right\}\quad \begin{aligned}&\text{T} = \text{abs. temp.}\\[2em] &p\ \text{in cm.}\end{aligned}$$

The values of the temperatures calculated from these equations are given above for the observed pressures. For the boiling-point we find by calculation

$$-\ 191\cdot47^\circ\ \text{C.},$$

while, for the triple-point, we have by observation

$$\text{Temperature} = -\ 205\cdot03^\circ\ \text{C., pressure} = 11\cdot486\ \text{cm.}$$

In the region covered by BALY and DONNAN's measurements the pressures are some 5 per cent. higher than theirs at corresponding temperatures, whereas they are some 8 to 10 per cent. lower than ESTREICHER and BOBOTEK's. The former give no criterion of the purity of their gas, and the latter's paper was not available. In the 'Table Annuaire de Constantes' this paper is quoted as giving a triple-point temperature of —207·0° C. and a pressure of 9·04 cm., with the melting-point at —205·7° C. Both these temperatures are much lower than those now determined, while the corresponding pressures are higher. It is extremely probable that any impurity present will lower the triple-point, and hence that ESTREICHER and BOBOTEK's results are vitiated by impurities.

The data for the melting-point curve of CO are contained in Table II. Over the range of pressures covered (0 to 205 atmospheres), a linear relation may be assumed to exist between pressure and temperature, and this may be expressed by the equation

$$t = -\ 205\cdot03 + 2\cdot25 \times 10^{-2}\ p.$$

TABLE II.—Carbon Monoxide—Melting-Point Curve.

Pressure. atms.	Temperature (observed).	Temperature (calculated).
	°	°
0·15	—205·03	(Triple-point)
55·53 ·53	—203·74 ·75	—203·78
103·86 ·86	—202·65 ·67	—202·69
157·06 ·06	—201·50 ·51	—201·50
205·44 ·44	—200·43 ·44	—200·41

(*b*) *Nitrogen.*—Triple-point and melting-point curve.

The vapour pressures of nitrogen have been accurately measured by P. G. CATH,*

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* 'Phys. Lab. Leiden, Commn.' No. 152d.

but the triple-point was derived by him only indirectly from the intersection of the vapour pressure curves of the liquid and solid phases. A determination now effected gave, as a mean of two very concordant direct observations,

Triple-point—
Temperature = — 209·95° C.
Pressure = 9·360 cm.

This agrees very satisfactorily with HOLST'S* recalculation of VON SIEMENS' result: — 209·92° C. and 9·35 cm.

The results obtained for the melting-point curve are reproduced in Table III, and the linear equation derived to express the relation between temperature and pressure is given by

$$t = -209 \cdot 95 + 2 \cdot 16 \times 10^{-2}\, p.$$

The increase in temperature with the pressure is thus almost identical for carbon monoxide and nitrogen.

TABLE III.—Nitrogen—Melting-point Curve.

Pressure. atms.	Temperature (observed).	Temperature (calculated).
	°	°
0·12	—209·95	(Triple-point)
55·46	—208·80	—208·75
·46	·81	
103·81	—207·72	—207·71
·81	·71	
157·03	—206·61	—206·56
·03	·56	
205·42	—205·45	—205·51
·42	·46	

§ 7. *Binary Systems.*

(*a*) *Carbon Monoxide-Nitrogen.*—As regards the liquid-vapour equilibria, only the points on the liquid branches of the liquid-vapour lenses are shown; the vapour points were very uncertain, as already stated, but the probable course of the vapour branches is indicated by dotted lines. The data for the liquid points, for four mixtures and three temperatures, are reproduced in Table IV, and the corresponding $p - x$ diagram shown in fig. 4.

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* 'Phys. Lab. Leiden, Commn.' No. 148.

TABLE IV.—Carbon Monoxide-Nitrogen—Liquid-vapour Equilibria.

CO 19·9 per cent. : N_2 80·1 per cent.		CO 40·05 per cent. : N_2 59·95 per cent.		CO 60·0 per cent. : N_2 40·0 per cent.		CO 79·95 per cent. : N_2 20·05 per cent.	
Pressure. cm.	Temperature.	Pressure. cm.	Temperature.	Pressure. cm.	Temperature.	Pressure. cm.	Temperature.
88·41	—193·88°	81·87	—193·90°	74·20	—193·90°	65·82	—193·90°
·38	·88	·89	·90	·29	·90	·94	·90
53·30	—198·13	49·00	—198·13	44·10	—198·13	38·81	—198·13
·20	·13	48·80	·12	43·80	·11	·81	·14
27·01	—203·07	24·60	—203·07	21·99	—203·07	18·94	—203·07
·04	·08	·63	·07	22·17	·06	19·02	·09

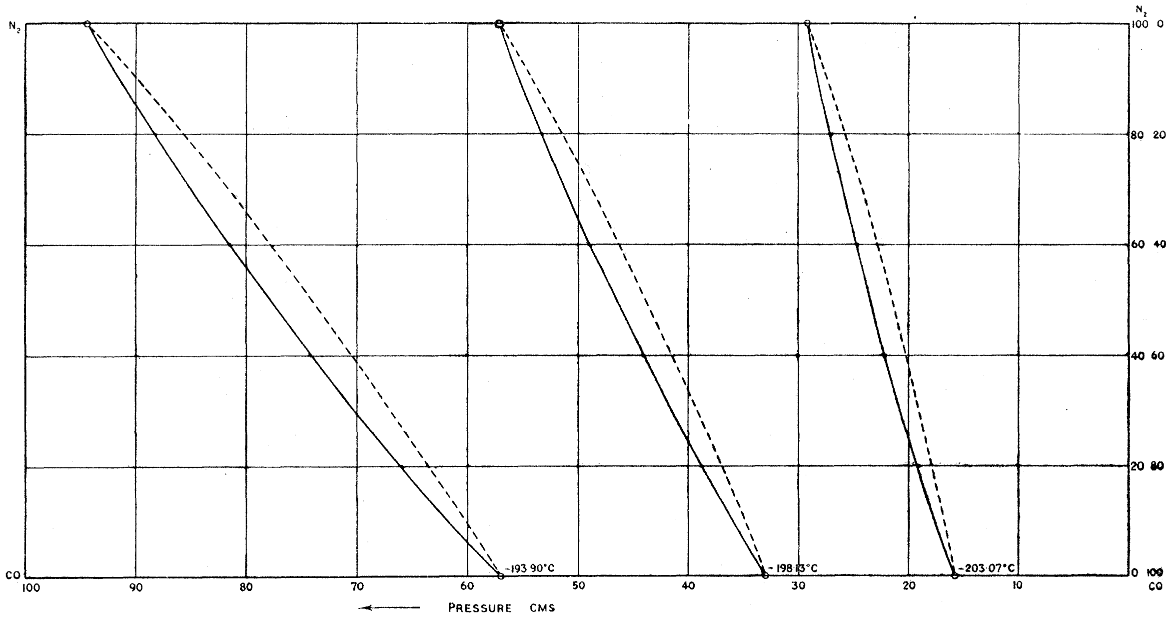

FIG. 4.—Carbon Monoxide-Nitrogen : $p - x$ Isotherms.

Data for the solid-liquid equilibria are limited to points on the freezing-point curve : they are contained in Table V. The freezing-point curve and the probable melting-point curve are shown in fig. 5. Finally, the three-phase curve, as derived from direct observation, is reproduced in fig. 6.

As might well be expected, the liquid-vapour lenses are very narrow and pursue an almost linear course, and it appears that, in the solid phase, a complete series of mixed crystals is formed. The form of the freezing-point curve should be noted, containing as it does a point of inflection. The same form is exhibited by the three-phase curve and it will be found to recur persistently in phase diagrams of the ternary system.

TABLE V.—Carbon Monoxide-Nitrogen—Solid-liquid Equilibria.

CO 19·9 per cent. : N_2 80·1 per cent.		CO 40·05 per cent. : N_2 59·95 per cent.		CO 60·0 per cent. : N_2 40·0 per cent.		CO 79·95 per cent. : N_2 20·05 per cent.	
Pressure. cm.	Temperature.	Pressure. cm.	Temperature.	Pressure. cm.	Temperature.	Pressure. cm.	Temperature.
10·04	—209·12°	10·87	—208·15°	11·22	—207·14°	11·94	—205·98°
·02	·05	·81	·14	·22	·10	·85	6·03

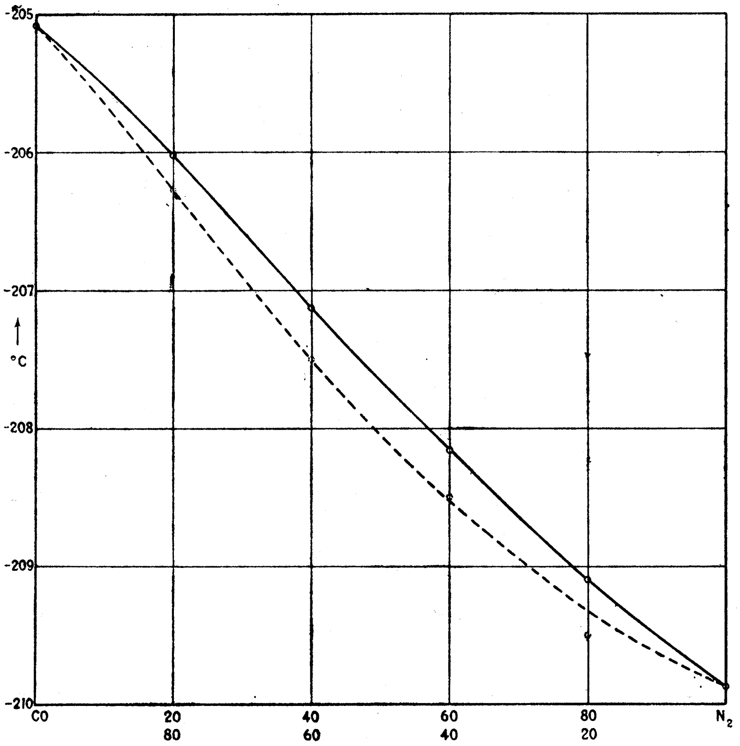

FIG. 5.—Carbon Monoxide-Nitrogen. Freezing-point and Melting-point Curves.

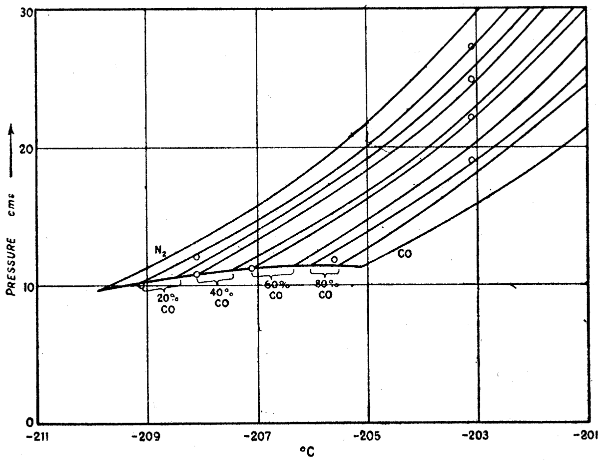

FIG. 6.—Carbon Monoxide-Nitrogen. Three-phase Curve.

(*b*) *Carbon Monoxide-Hydrogen.*—(i) The one series of results obtained for this system, at a temperature of —185° C., by the very laborious volumetric method, is reproduced in Table VI, and the corresponding $p - x$ diagram is drawn in fig. 7, the points being indicated by triangles. The points shown in the table and the figure are derived from no fewer than 271 pressure-volume determinations: the temperature was throughout within 0·03° of —185° C. The observations with the mixture containing 10 per cent. carbon monoxide are little better than estimates, for the breaks in the isotherms are too slight to allow of an exact determination of the border points. Apart from this mixture, however, the results may be regarded as being reasonably accurate.

TABLE VI.—Carbon Monoxide-Hydrogen—$p - x$ Isotherm at —185° C.

Mixture per cent. CO.	Lower point. atms.	Higher point. atms.
100	2·18	
90	—	46·8
75	—	111·4
60	—	163·7
50	—	183·6
40	—	187·0
30	7·7	181·9
20	12·3	162·5
15	—	122·7
10	22·8	(59·5)

From fig. 7 it appears that, for a temperature of —185° C., the plait-point lies at 187·5 atmospheres, the mixture containing about 42 per cent. CO; whilst the critical point of contact is situated (very approximately) at 55 atmospheres, the mixture containing 10 per cent. CO.

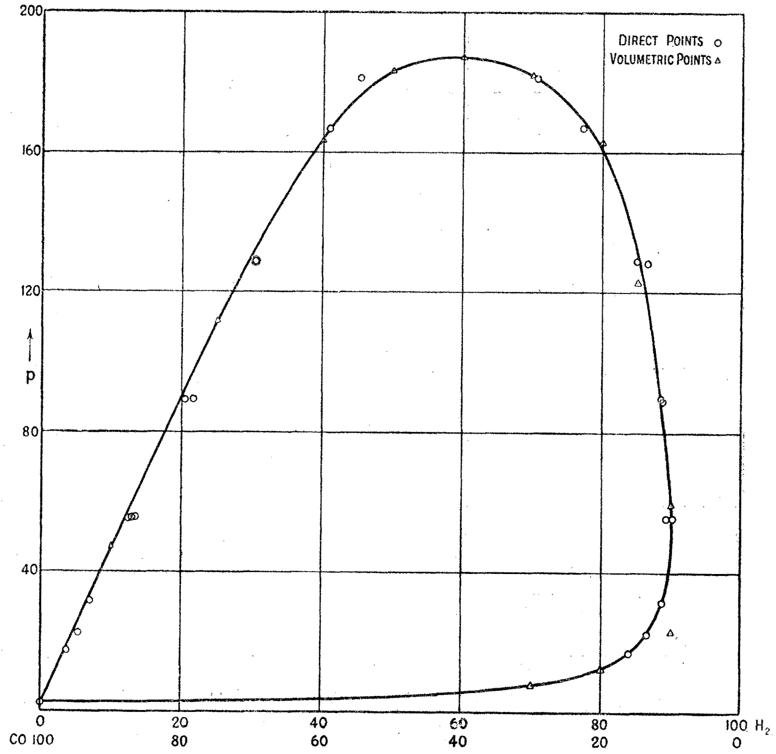

FIG. 7.—Carbon Monoxide-Hydrogen. $p - x$ Isotherm at —185° C.

A large number of measurements were made at —200° C., but owing to the fact that the great expansion in the loop at that temperature was not realised, search was made for the border curve in an impossible region. Two points on the $p - x$ loop were however, determined, and these are of interest in connection with the results obtained by the entirely different analytical method, to be discussed next. They were :—

90 per cent. CO	62·5 atmospheres.
10 per cent. CO	8·0 atmospheres.

(ii) The results obtained by the analytical method for the liquid-vapour equilibria are reproduced in Tables VII to X ; points marked with asterisks in Tables VII to IX indicate that the dead spaces in the sampling taps were "washed out" before sampling ; this procedure was adopted throughout the determinations of Table X and subsequently. To economise space, only the $p - x$ isotherms at —185° and —200° C. have been reproduced, in figs. 7 and 8, and the points obtained by the volumetric method are also plotted ; it will be seen that the agreement is very satisfactory. The lack of concordance among some of the liquid points at the higher temperatures is almost certainly due to the failure to wash out the dead spaces.

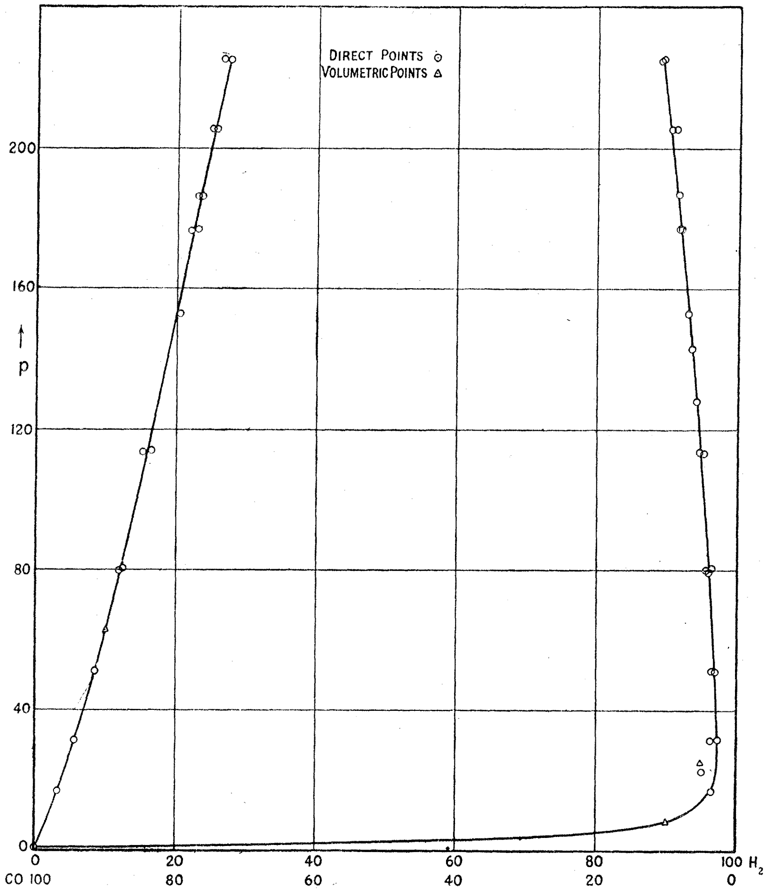

Fig. 8.—Carbon Monoxide-Hydrogen. $p - x$ Isotherm at —200° C.

TABLE VII.—Carbon Monoxide-Hydrogen—$p - x$ Isotherm at —185° C.

Temperature.	Pressure. atms.	Liquid per cent. H_2.	Vapour per cent. H_2.
—185·00°	181·3	45·4	70·4
·01	166·7	41·0	77·1
·03	128·2	30·3	84·8
$\cdot\overline{99}$	·1	30·4	—
·00	·0	—	86·7
·02	89·6	21·7	88·7
$\cdot\overline{99}$	·3	20·3	88·8
·01*	55·9	13·4	90·2
·00	·8	12·9	89·3
·00	·4	12·6	—
·00	31·4	7·1	88·8
·00	22·1	5·2	86·6
·02*	17·2	3·6	84·0
·00	2·18	0·0	0·0

TABLE VIII.—Carbon Monoxide-Hydrogen—$p - x$ Isotherm at —190° C.

Temperature.	Pressure. atms.	Liquid per cent. H_2.	Vapour per cent. H_2.
—190·02°	224·8	54·1	66·3
·03	220·9	48·6	69·4
·00	215·2	(38·9)	72·5
·04	·1	47·0	73·7
$\cdot\overline{98}$	210·4	44·8	75·9
·02	205·4	42·2	(73·5)
·04	·4	43·0	(80·0)
·00	·4	43·5	76·6
·01	200·6	41·1	76·7
·02	·6	41·5	77·7
·00	195·8	40·1	79·5
·01	190·9	38·1	80·5
·02	186·1	36·8	80·8
·00	176·4	34·4	83·1
·02	166·8	32·9	84·3
$\cdot\overline{97}$	·7	(29·2)	84·0
·02*	128·1	24·9	88·9
·00	·1	25·4	88·8
·02	109·8	22·8	90·4
·02*	·8	21·0	90·7
·02	·6	20·6	90·6
$\cdot\overline{99}$*	89·3	17·0	92·0
·01	·5	19·5	91·8
·01	51·2	12·5	93·2
·02*	·2	10·2	93·1
·02	17·2	2·7	89·9
·00	1·18	0·00	0·0

Table IX.—Carbon Monoxide-Hydrogen—$p - x$ Isotherm at —200° C.

Temperature.	Pressure. atms.	Liquid per cent. H_2.	Vapour per cent. H_2.
—200·$\bar{9}\bar{9}$°*	224·9	27·5	89·0
·00	·8	26·5	89·3
·03	205·6	25·0	91·2
·03	·4	25·7	90·2
·00	186·2	22·9	91·6
·03	·2	23·6	91·4
·01	176·4	23·0	92·0
·$\bar{9}\bar{6}$*	·4	21·8	91·7
·00	152·4	—	93·1
·03	·4	20·6	93·0
·$\bar{9}\bar{9}$	142·5	—	93·5
·01	128·0	—	94·2
·01	113·9	16·6	95·1
·00	·8	15·4	95·5
·$\bar{9}\bar{8}$*	·7	16·5	94·8
·00	80·2	12·7	95·9
·01*	·1	12·0	96·4
·$\bar{9}\bar{8}$	79·7	—	96·3
·01	51·0	8·4	96·7
·00	50·9	—	97·0
·01*	31·8	5·6	97·5
·01	31·5	—	96·4
·01	22·2	—	95·4
·$\bar{9}\bar{8}$*	17·3	3·3	96·7
·00	0·33	0·0	0·0

Table X.—Carbon Monoxide-Hydrogen—$p - x$ Isotherm at —205° C.

Temperature.	Pressure. atms.	Liquid per cent. H_2.	Vapour per cent. H_2.
—205·01°	215·16	20·2	93·4
·00	190·97	18·8	93·9
·00	152·33	16·3	94·6
·00	·17	15·8	(96·8)
·00	118·38	13·8	96·5
·$\bar{9}\bar{9}$	·29	—	96·2
·01	79·89	10·2	97·7
·01	·86	—	97·7
·00	41·45	6·3	97·5
·00	·41	6·2	98·5
·04	·26	—	98·7
·00	31·67	4·9	98·6
·00	26·61	4·2	97·6
·$\bar{9}\bar{8}$	21·69	3·3	98·2
·$\bar{9}\bar{6}$	17·02	3·0	97·9

A summary of the critical constants for the four temperatures investigated is given in Table XI. Where the figures are estimated, they are placed in parentheses.

TABLE XI.—Carbon Monoxide-Hydrogen—Critical Constants.

Temperature.	Plait-point.		Critical point of contact.	
	Pressure. atms.	Per cent. H_2.	Pressure. atms.	Per cent. H_2.
—185°	187	58	54	90
—190	228	60	48	93
—200	(325)	(64)	34	$97\frac{1}{2}$
—205	(380)	(66)	30	$99\frac{1}{2}$

(iii) Tables XII and XIII contain the compositions of the vapour in equilibrium with the solid phase at —210° and —215° C. respectively. The results are quite satisfactory. The $p - x$ diagram at —210° C. is shown in fig. 9.

TABLE XII.—Carbon Monoxide-Hydrogen—Vapour Phase at —210° C.

Temperature.	Pressure. atms.	Per cent. H_2.
$-210\cdot\bar{9}\bar{8}^\circ$	195·75	96·31
·01	176·41	96·53
$\cdot\bar{9}\bar{8}$	147·39	96·88
·00	137·76	97·03
·00	104·01	97·80
·00	79·80	97·42
·02	65·74	98·76
·03	32·03	99·18
·02	21·85	99·12
·00	16·81	99·22

TABLE XIII.—Carbon Monoxide-Hydrogen—Vapour Phase at —215° C.

Temperature.	Pressure. atms.	Per cent. H_2.
$-215\cdot\bar{9}\bar{5}^\circ$	176·37	98·18
$\cdot\bar{9}\bar{4}$	157·03	98·08
$\cdot\bar{9}\bar{3}$	128·05	98·50
$\cdot\bar{9}\bar{4}$	89·52	98·90
·01	51·37	99·47

Points on the three-phase curve are contained in Table XIV, and the three-phase curve itself is drawn in fig. 10. It will be seen that the agreement between the individual points is not very good.

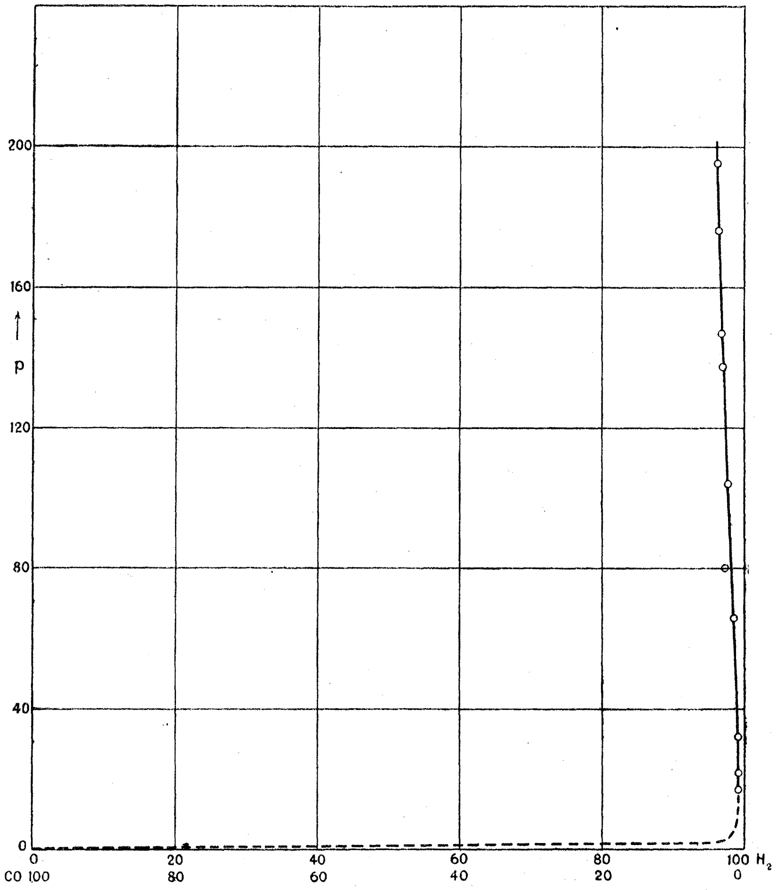

FIG. 9.—Carbon Monoxide-Hydrogen.
$p - x$ Isotherm at —210° C.

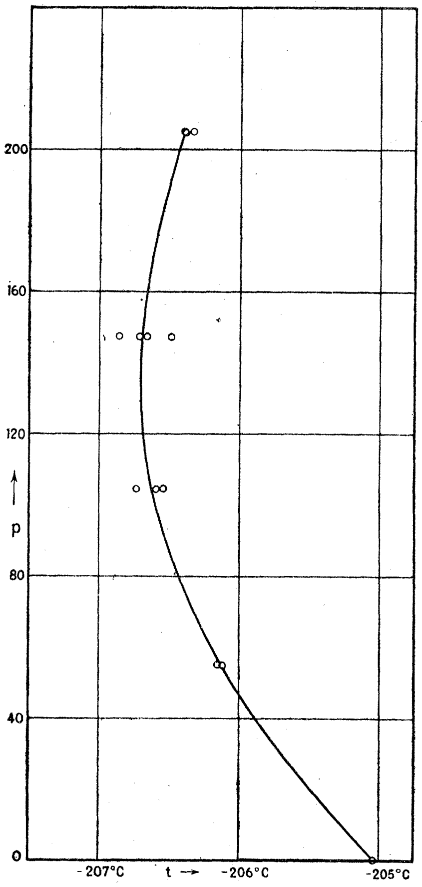

FIG. 10.—Carbon Monoxide-Hydrogen.
Three-phase Curve.

TABLE XIV.—Carbon Monoxide-Hydrogen—Three-phase Curve.

Pressure. atms	Temperature.	Pressure. atms.	Temperature.
55·2	—206·12°	147·4	—206·48°
·2	·15	·4	·67
104·1	—206·54	·4	·72
·1	·59	·4	·87
·1	·73	205·5	—206·34
		·5	·38
		·5	·39

Finally, fig. 11 shows the isobars at 30, 120 and 200 atmospheres between temperatures of —160° and —215° C. Experimentally determined points and portions of the curves are shown in full; the interpolated portions are dotted. It has been assumed—not very probably—that mixed crystals are not formed.

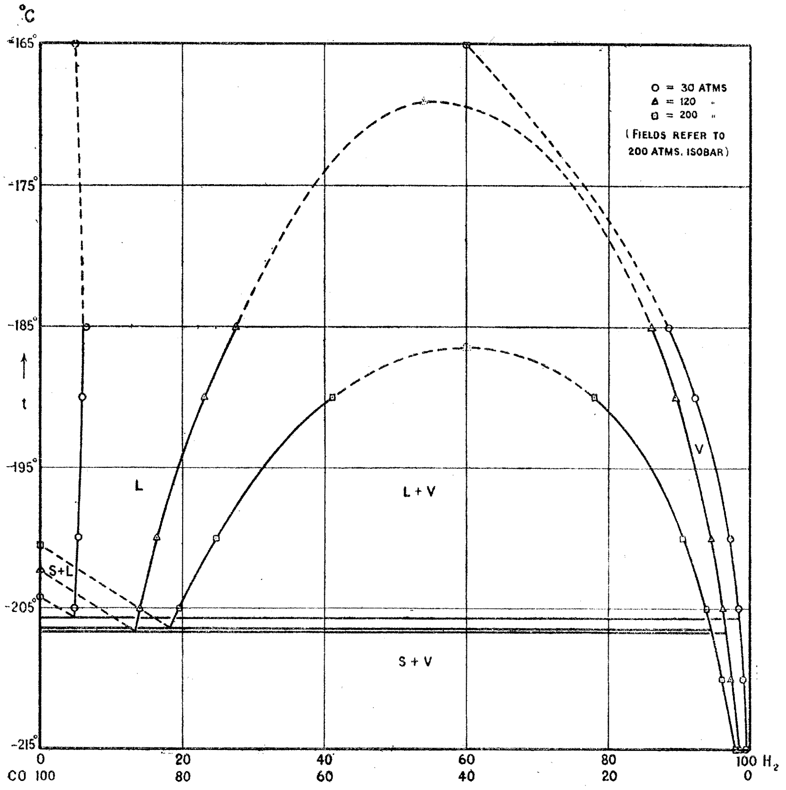

FIG. 11.—Carbon Monoxide-Hydrogen. $t - x$ Isobars at 30, 120 and 200 atms.

(*c*) *Nitrogen-Hydrogen.*—(i) The experimental data for the isotherms of the binary system nitrogen-hydrogen at —185°, —195°, —205°, and —210° C. (all liquid-vapour equilibria) are contained in Tables XV to XVIII, and the isotherms at —185°, —195°, and —210° C. are reproduced in figs. 12 to 14. The results are uniformly satisfactory,

TABLE XV.—Nitrogen-Hydrogen—$p - x$ Isotherm at —185° C.

Temperature.	Pressure. atms.	Liquid per cent. H_2.	Vapour per cent. H_2.
—185·01°	137·73	47·0	50·8
·02	132·81	42·0	71·2
·00	128·08	38·7	74·5
·02	118·34	34·5	78·3
·00	104·00	28·3	82·1
·01	80·00	20·7	86·6
·01	56·09	—	86·2
·02	41·04	9·2	85·3
·01	26·76	5·3	83·3
·99	17·01	2·4	77·0
·00	2·39	0·0	0·0

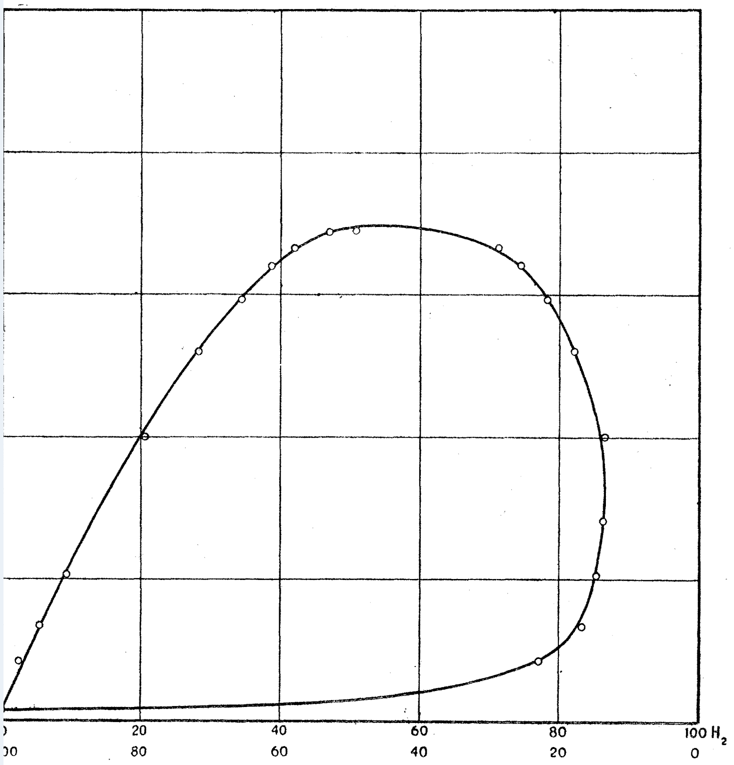

FIG. 12.—Nitrogen-Hydrogen. $p - x$ Isotherm at —185° C.

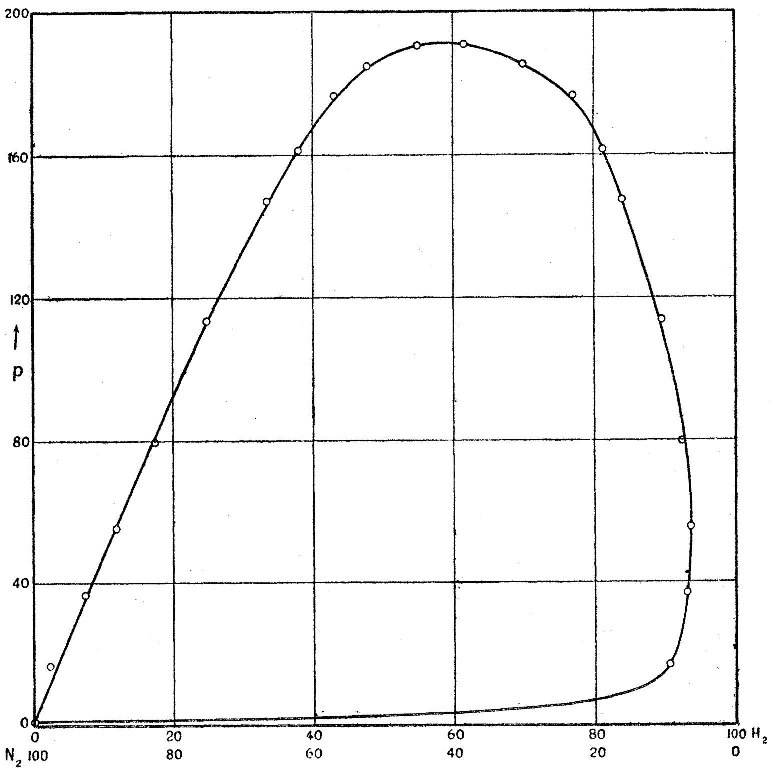

FIG. 13.—Nitrogen-Hydrogen. $p - x$ Isotherm at —195° C.

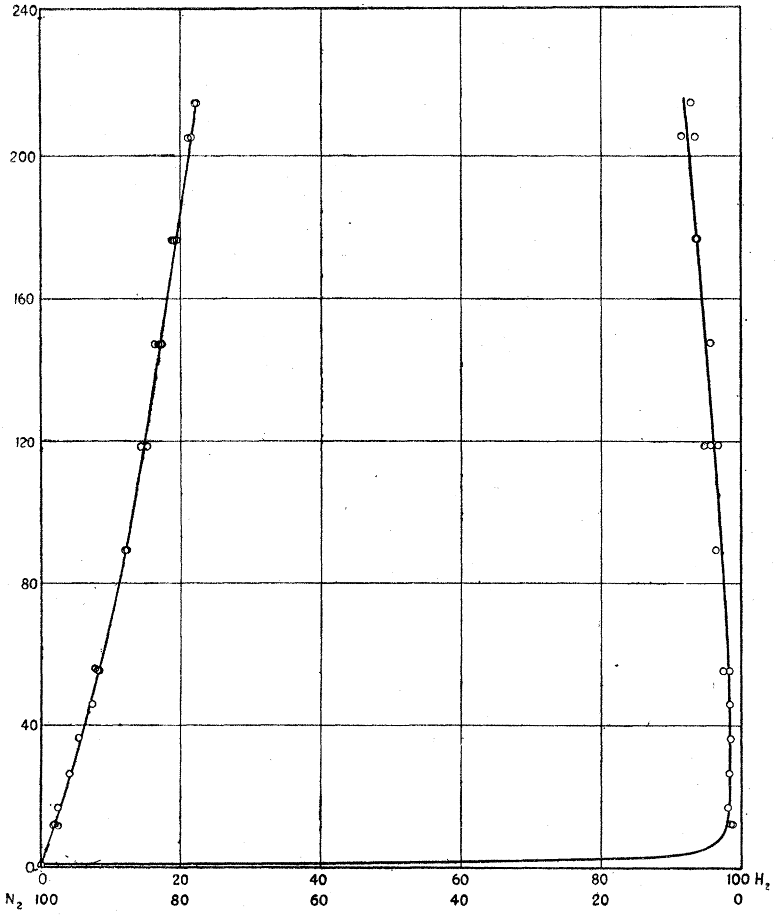

FIG. 14.—Nitrogen-Hydrogen. $p - x$ Isotherm at —210° C.

TABLE XVI.—Nitrogen-Hydrogen—$p - x$ Isotherm at —195° C.

Temperature.	Pressure. atms.	Liquid per cent. H_2.	Vapour per cent. H_2.
—195·00°	190·89	54·9	61·7
·02	185·08	47·9	70·0
·03	176·63	43·0	75·9
·02	161·88	37·9	81·3
·01	147·37	33·4	84·0
·02	113·60	24·8	89·5
·02	79·90	17·5	92·2
·02	55·56	11·9	93·7
·01	36·59	7·3	93·0
·02	17·19	2·3	90·5
·00	1·10	0·0	0·0

TABLE XVII.—Nitrogen-Hydrogen—$p - x$ Isotherm at —205° C.

Temperature.	Pressure. atms.	Liquid per cent. H_2.	Vapour per cent. H_2.
—205·03°	224·81	31·1	85·4
·01	222·84	30·7	88·1
·03	210·28	29·6	88·3
·04	209·28	29·6	87·0
·01	176·40	25·2	90·3
·01	147·44	22·0	90·8
·03	·41	21·9	92·2
·05	118·47	18·1	94·4
·03	89·67	14·7	95·3
·05	·55	15·4	95·5
·05	55·88	9·4	97·3
·00	45·89	7·6	97·9
·03	35·98	6·6	97·6
·01	26·58	4·6	97·6
·03	17·19	3·3	97·3
·00	0·29	0·0	0·0

TABLE XVIII.—Nitrogen-Hydrogen—$p - x$ Isotherm at —210° C.

Temperature.	Pressure. atms.	Liquid per cent. H_2.	Vapour per cent. H_2.
—210·01°	215·12	22·2	92·9
·01	·12	22·1	—
$\cdot\overline{99}$	205·46	21·6	93·5
$\cdot\overline{99}$	·41	21·0	91·5
·03	176·43	18·9	93·7
·00	·40	19·5	93·3
$\cdot\overline{99}$	·40	19·1	—

TABLE XVIII (continued).

Temperature.	Pressure. atms.	Liquid per cent. H_2.	Vapour per cent. H_2.
—·00	147·44	16·8	—
$\cdot\overline{99}$	·41	17·3	—
$\cdot\overline{98}$	·40	17·2	95·7
$\cdot\overline{99}$	·35	16·3	—
·00	118·48	14·6	96·8
$\cdot\overline{99}$	·45	15·2	—
·00	·44	14·7	95·7
$\cdot\overline{99}$	·41	14·3	94·8
·01	89·58	12·0	96·3
$\cdot\overline{99}$	·55	12·1	—
·00	56·03	7·8	—
·00	55·59	8·5	97·4
·00	·50	8·3	98·4
$\cdot\overline{98}$	46·11	7·5	98·2
$\cdot\overline{98}$	36·30	5·7	98·4
$\cdot\overline{99}$	26·70	4·1	98·1
·00	17·09	2·7	98·0
$\cdot\overline{99}$	12·21	2·5	98·4
$\cdot\overline{98}$	·19	1·9	—
·00	·15	2·0	98·7
·00	0·12	0·0	0·0

except at —210°, where some trouble was experienced with leakages through the gland of the vapour sampling tap ; on that account, some of the vapour analyses are omitted in Table XVIII.

The critical constants, as derived from the $p - x$ isotherms, are given in Table XIX.

TABLE XIX.—Nitrogen-Hydrogen—Critical Constants.

Temperature.	Plait-point.		Critical point of contact.	
	Pressure. atms.	Per cent. H_2.	Pressure. atms.	Per cent. H_2.
—185°	138	53	60	87
—195	191	58	50	93½
—205	(340)	—	35	98
—210	—	—	25	98½

(ii) The compositions of the vapour in equilibrium with the solid phase at —212·5° and —215° C. are contained in Tables XX and XXI, and the isotherm at —215° is plotted in fig. 15. The pumping off of the vapour samples is reflected in the improved concordance of the results.

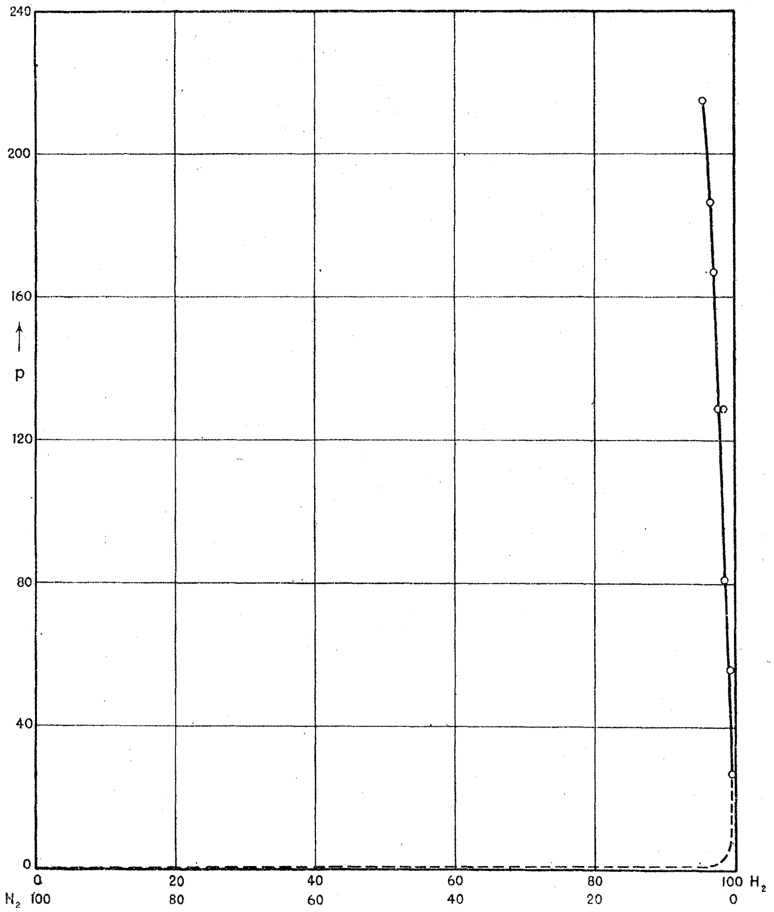

Fig. 15.—Nitrogen-Hydrogen. $p - x$ Isotherm at —215° C.

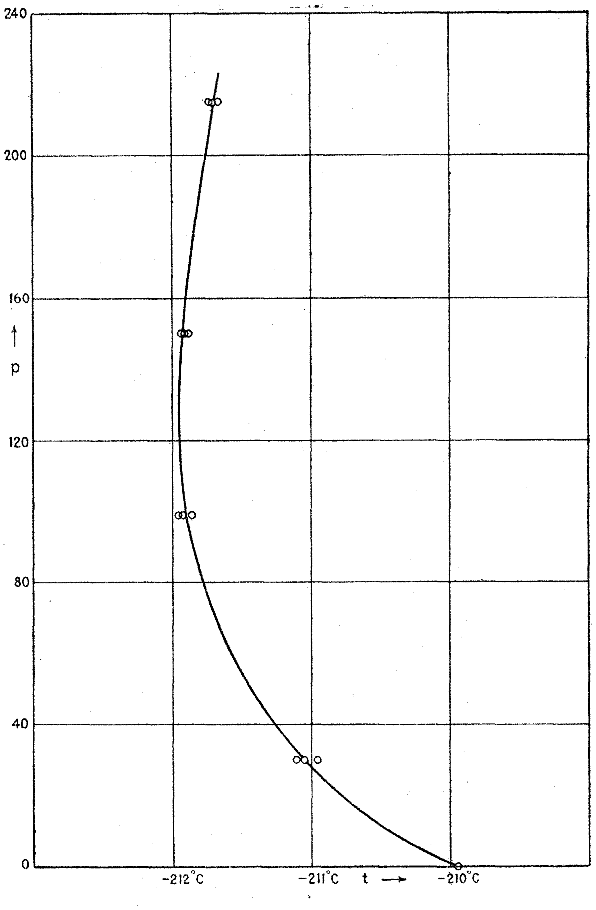

Fig. 16.—Nitrogen-Hydrogen. Three-phase Curve.

Table XX.—Nitrogen-Hydrogen—Vapour-phase at —212·5° C.

Temperature.	Pressure. atms.	Per cent. H_2.
—212·48°	205·45	92·81
·48	186·05	95·24
·49	·05	94·82
·49	176·39	95·26
·48	·38	95·36
·46	166·77	95·40
·49	128·15	96·72
·46	·15	96·16
·48	104·18	97·67
·47*	·07	97·42
·47	89·61	96·79
·48	56·22	98·62
·49	51·96	99·22
·51	40·44	99·11
·46	17·47	98·71

* Mean of four very concordant readings.

TABLE XXI.—Nitrogen-Hydrogen—Vapour Phase at —215° C.

Temperature.	Pressure. atms.	Per cent. H_2.
—215·$\overline{98}$°	215·16	95·63
·$\overline{97}$	186·14	96·54
·$\overline{98}$	166·80	97·03
·$\overline{99}$	128·22	98·15
·00	·19	97·58
·00	80·22	98·36
·01	55·95	99·22
·01	26·74	99·66

Points on the three-phase curve are contained in Table XXII, and the curve itself is shown in fig. 16 ; it will be seen that the agreement between the points is considerably better than in the case of the carbon monoxide-hydrogen system.

Finally, isobars at 30, 120 and 200 atmospheres between temperatures of —165° and —215° C. are reproduced in fig. 17, which may be compared with fig. 11.

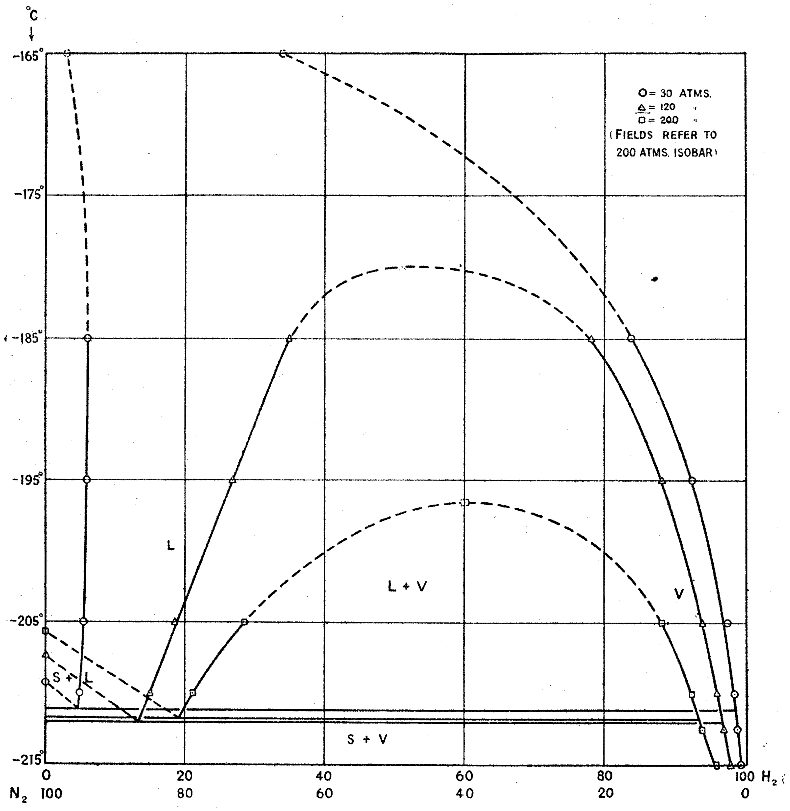

FIG. 17.—Nitrogen-Hydrogen. $t - x$ Isobars at 30, 120 and 200 atms.

TABLE XXII.—Nitrogen-Hydrogen—Three-phase Curve.

Pressure. atms.	Temperature.	Pressure. atms.	Temperature.
29·8	—211·06°	150·3	—211·91°
·8	·$\overline{96}$	·5	·93
·8	·12	·5	·89
99·0	—211·96	215·2	—211·75
·0	·93	·2	·68
·0	·87	·2	·71

§ 8. *The Ternary System.*

The ternary system was investigated at pressures of 30, 90, and 150 atmospheres, and at temperatures of —185°, —195°, and —205° C. It has not been considered necessary to reproduce the numerous experimental data, but it may be noted that the largest pressure and temperature deviations were 0·4 atmospheres and 0·06° respectively, the consequent errors being much less than those of sampling. Graphical representations of the equilibria in the customary triangular diagrams are reproduced in figs. 18 to 26; in the last figure (fig. 26), however, the vapour points are too close together

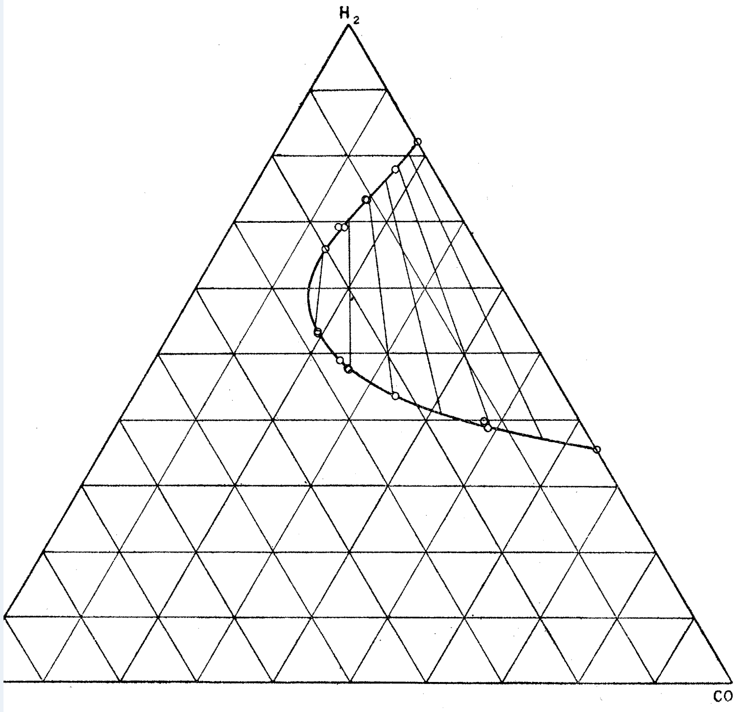

FIG. 18.—Carbon Monoxide-Nitrogen-Hydrogen. Equilibrium at —185° C. and 150 atms.

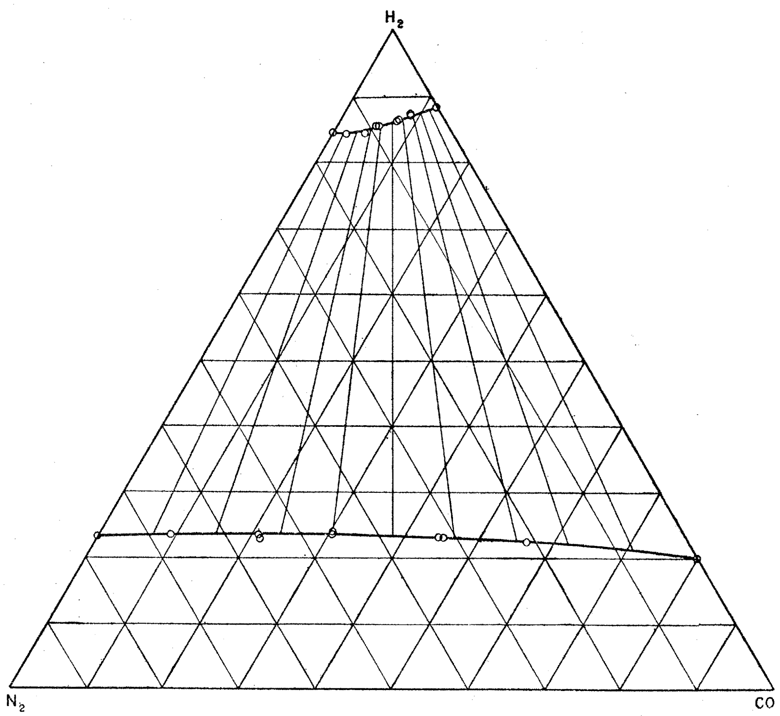

FIG. 19.—Carbon Monoxide-Nitrogen-Hydrogen. Equilibrium at —185° C. and 90 atms.

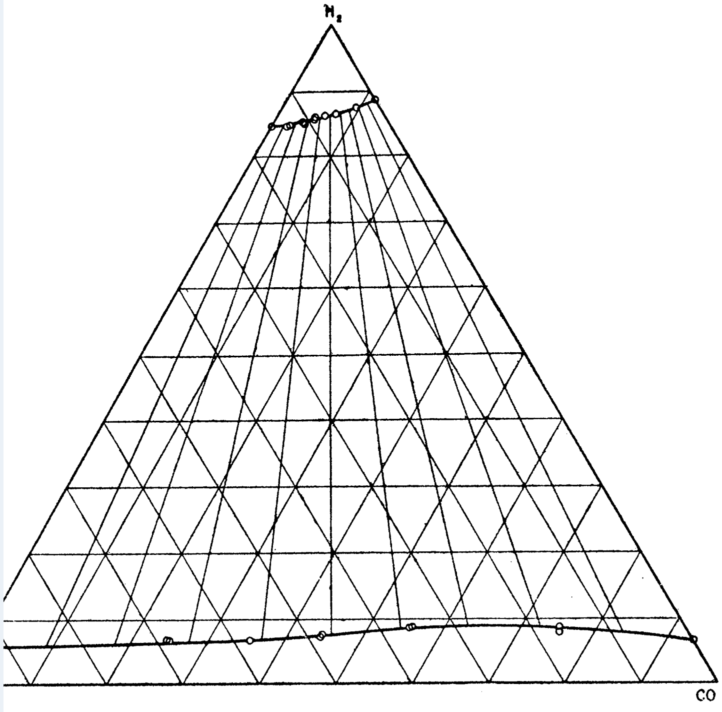

FIG. 20.—Carbon Monoxide-Nitrogen-Hydrogen. Equilibrium at —185° C. and 30 atms.

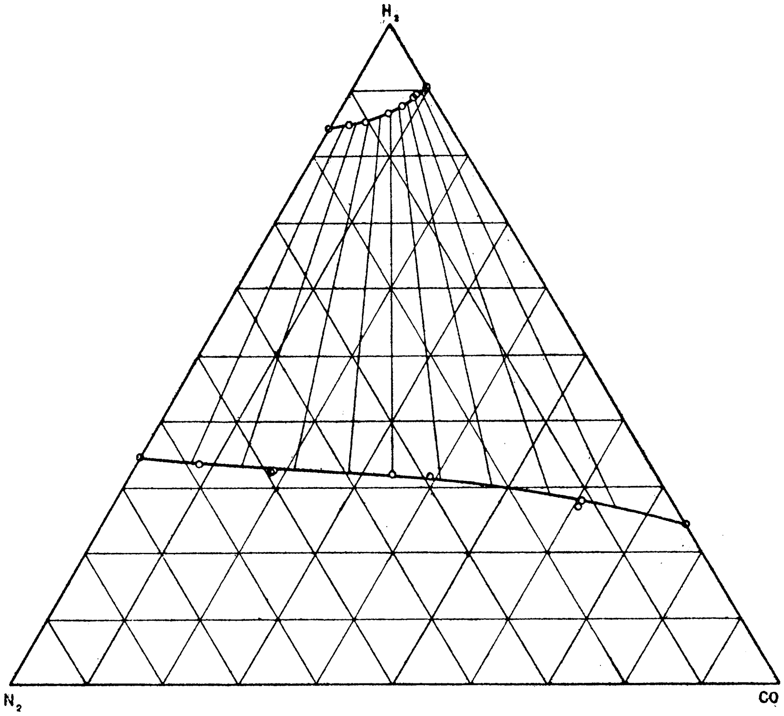

FIG. 21.—Carbon Monoxide-Nitrogen-Hydrogen. Equilibrium at —195° C. and 150 atms.

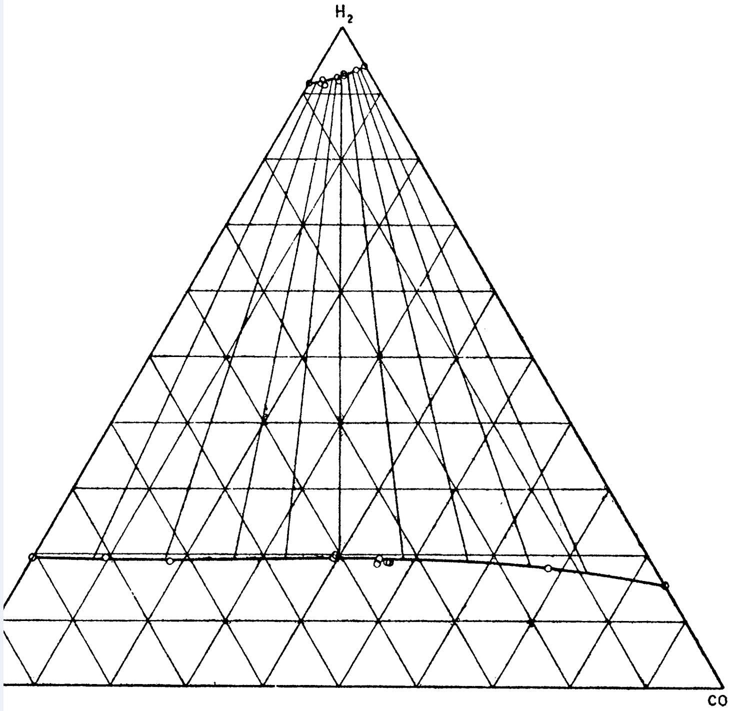

FIG. 22.—Carbon Monoxide-Nitrogen-Hydrogen. Equilibrium at —195° C. and 90 atms.

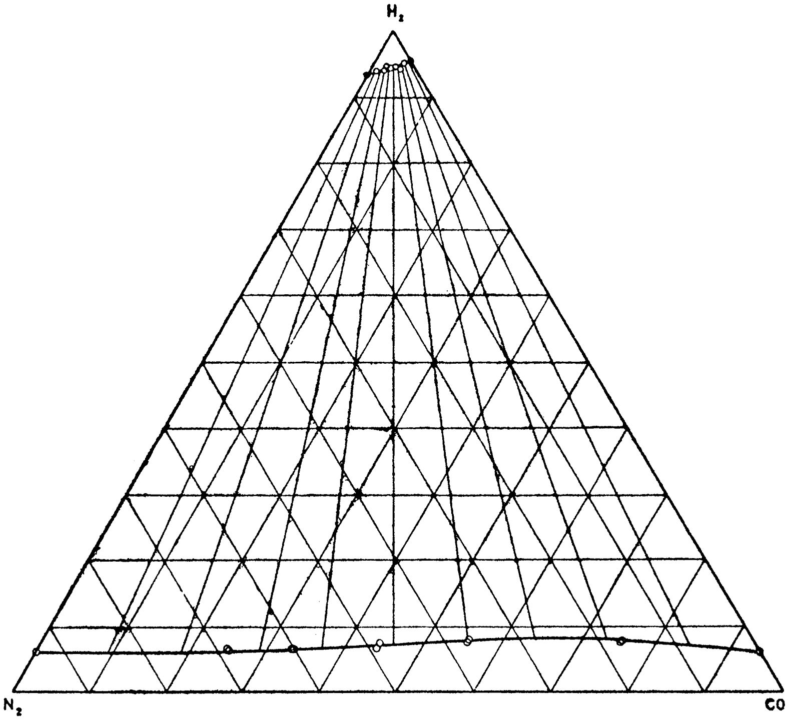

FIG. 23.—Carbon Monoxide-Nitrogen-Hydrogen. Equilibrium at —195° C. and 30 atms.

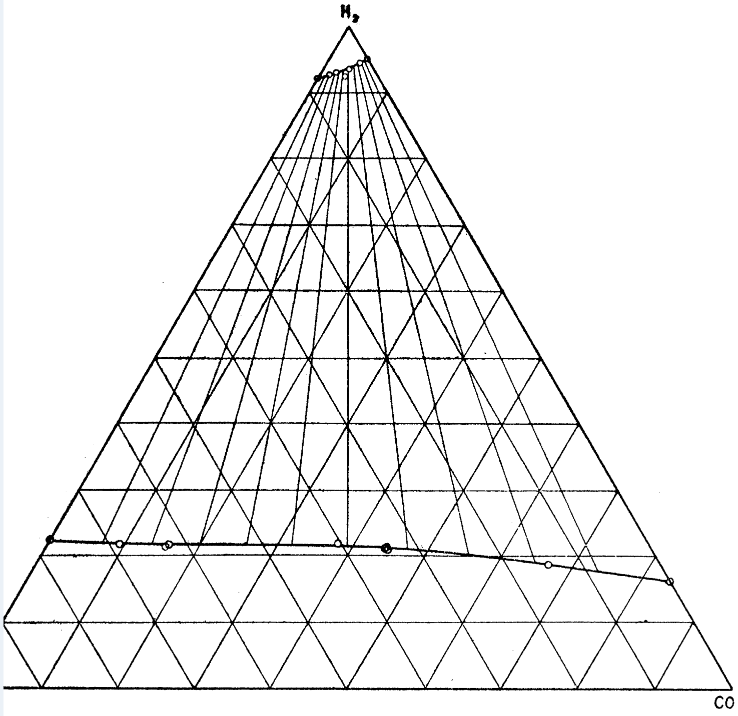

FIG. 24.—Carbon Monoxide-Nitrogen-Hydrogen. Equilibrium at —205° C. and 150 atms.

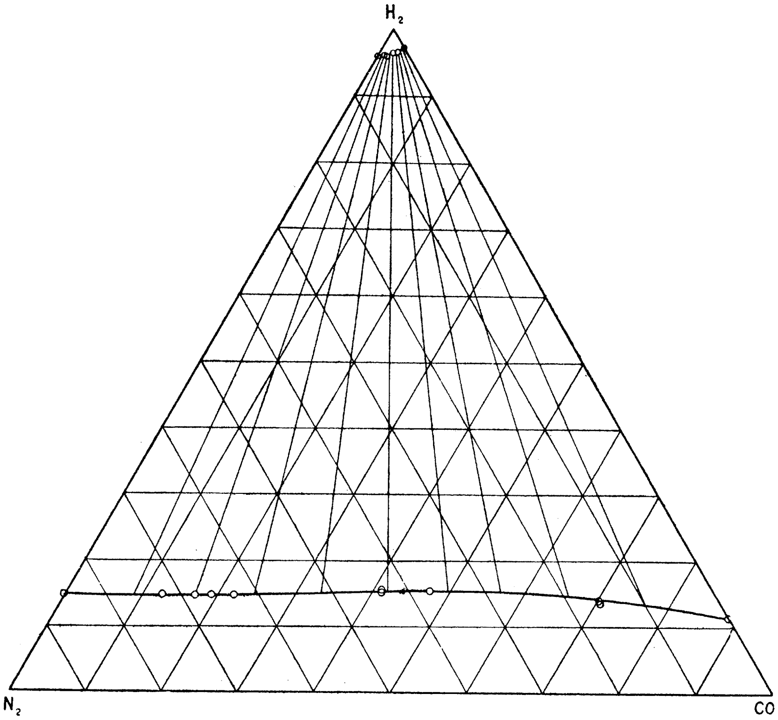

FIG. 25.—Carbon Monoxide-Nitrogen-Hydrogen. Equilibrium at —205° C. and 90 atms.

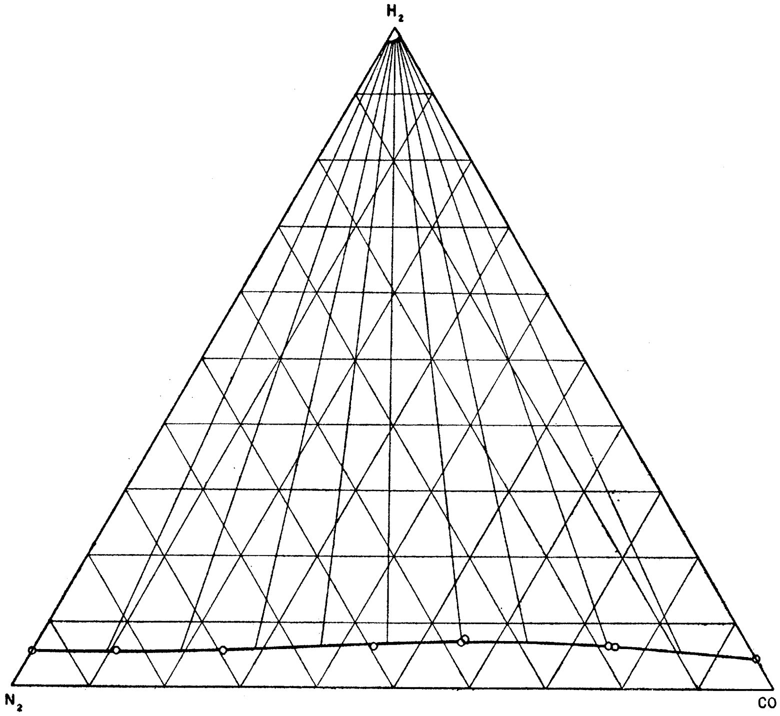

FIG. 26.—Carbon Monoxide-Nitrogen-Hydrogen. Equilibrium at —205° C. and 30 atms.

to be individually plotted. Tie-lines have been drawn in all the diagrams for every 10 per cent. difference in the carbon monoxide-nitrogen ratio. These lines have been obtained by calculating the ratio both for the liquid and for the vapour, plotting one value against the other, and then drawing a smooth curve through the points so obtained. At the two lower temperatures and pressures, the total percentage of carbon monoxide and nitrogen in the vapour is small, so that the ratio is liable to large errors; the general course of the ratio curve, however, is unlikely to differ appreciably from the more accurately determined course at the higher temperature and pressure.

At 150 atmospheres and —185° C., we find a plait-point for a mixture of the approximate composition 15 per cent. CO, 25 per cent. N_2, 60 per cent. H_2, whereas, for all the other conditions of pressure and temperature investigated, two phases are present throughout.

It is of interest to note that all the liquid branches (and all the carbon monoxide-nitrogen ratio curves) exhibit a point of inflection, just as was found in the case of the freezing-point curve for mixtures of carbon monoxide and nitrogen at low pressures.

An inspection of figs. 18 to 26 shows that the conditions for the separation of hydrogen from the ternary mixture are invariably slightly less favourable than if the ternary system were a linear function of the two corresponding binary systems, for the vapour branch is slightly concave to the hydrogen apex, and the liquid branch is concave to the base. The divergences from linear relations are, however, relatively small.

Summary.

§ 1. Apart from the system oxygen-nitrogen, no account appears to have been published of work on any binary system at low temperatures and high pressures. No ternary system seems to have been investigated under these conditions.

§ 2. The apparatus employed in the present research is described.

§ 3. The mode of preparation of the gases used is outlined.

§ 4. A description is given of the various experimental methods developed. Particular attention is devoted to the analytical method of determining liquid-vapour equilibria, by which most of the experimental data was obtained.

§ 5. Sources of errors, and their probable effect, are discussed.

§ 6. A few constants are determined for carbon monoxide and nitrogen, viz., the triple-point and the melting-point curve (up to a pressure of 205 atmospheres) and, in the case of carbon monoxide, the vapour pressures below 2 atmospheres.

§ 7. In the binary system carbon monoxide-nitrogen, the liquid branches of the isotherms at —193·90°, —198·13° and —203·07° are determined, and the freezing-point curve is also derived, although the method employed is not very satisfactory.

Tables of experimental data for the isotherms at —185°, —190°, —200°, —205°, —210° and —215° C., as found by the analytical method, and at —185° C., as confirmed

by the volumetric method, are given for the system carbon monoxide-hydrogen; the three-phase curve is also derived. In each case the pressures range up to 225 atmospheres.

Similar data, as found by the analytical method, are reproduced for the system nitrogen-hydrogen, at temperatures of —185°, —195°, —205°, —210°, —212·5° and —215° C.

§ 8. Equilibria in the ternary system carbon monoxide-nitrogen-hydrogen are investigated at pressures of 30, 90 and 150 atmospheres, and at temperatures of —185°, —195°, and —205° C.

As was stated in the Introduction, the design of the cryogenic installation employed in the present research is based on that in use at the Physical Laboratory at the University of Leiden, where, by the kind invitation of the late Professor KAMERLINGH ONNES and of Dr. C. A. CROMMELIN, the author was able to learn the necessary technique. Apart from machines and instruments of standard pattern, the whole of the apparatus was constructed by Messrs. H. J. WELBERGEN (glass-blower) and J. PONT (fine mechanic). Messrs. H. RYDER and J. C. JOHNSON assisted throughout with the determinations and computations, and many of the analyses were carried out by Messrs. M. JONES and E. HATTON.

Finally, the author desires to offer his grateful thanks to the late Rt. Hon. Lord MELCHETT, F.R.S., to the Directors of Messrs. IMPERIAL CHEMICAL INDUSTRIES, LTD., and to Major F. A. FREETH, F.R.S., for their kind permission to publish this paper.