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GESELLSCHAFT FUR LINDE'S EISMACHINEN
HOLLRIEGELSKREUTH

Weir, H. M.

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

RESTRICTED

REPORT ON
GESELLSCHAFT FUR LINDE'S EISMACHINEN A. G. AT
HOLLRIEGELSKREUTH, NEAR MUNCHEN, GERMANY

Reported by:

H. M. Weir U.S.

on behalf of the

British Ministry of Fuel and Power
and
U.S. Technical Industrial Intelligence Committee

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VISIT TO GESELLSCHAFT FÜR LINDE'S EISMACHINEN A.G.
NEAR MÜNCHEN

A. INTRODUCTION, AND PERSONNEL INTERROGATION

On May 23 and again on May 30, 1945, the plant at Hüllriegelskreuth, near München, Germany, of the Linde Company, officially the "Gesellschaft für Linde's Eismaschinen A.G.", was visited by Mr. L. L. Newman and Dr. H. M. Weir. Dr. Richard Linde furnished most of the information on both occasions, though Dr. Friedrich Linde, his brother, and Dr. Ing. Ulrich Hailer, Chief Engineer, were present at the first discussion.

B. GENERAL HISTORY OF LINDE CO. ACTIVITIES

The Linde Company, founded in 1879, makes equipment, both large and small, covering the entire field of temperatures below normal. Branches at other points in Germany manufacture compressors for all gases and pressures, high pressure valves, gas cylinders, and compressed air tools of various kinds. Another subsidiary, Guldner Motoren Werke in Asschaffenburg, makes four stroke cycle diesel engines of most varied kinds. Aside from these main avenues of effort, the company makes or markets nearly all the accessories which go with the main items of manufacture. As might be surmised, the Company was very busy during the war period.

The present manuscript summarizes discussion on the commercial manufacture of oxygen (and nitrogen), and on the low temperature separation of hydrocarbon gases. The latter field has obvious interest to petroleum technologists, and the production of oxygen is, of course, of interest inasmuch as there are certain new processes for the manufacture of gas-suitable for Fischer-Tropsch synthesis or hydrogenation--which make use of oxygen instead of air in primary gas producers.

The liquefaction of air was first accomplished in a fashion giving promise of commercial utilization by Carl von Linde, father of the above-mentioned Linde brothers. Strides were made technically in the low temperature field in the 80's up to about 1910, but the scale of plants manufactured was small. The first really large scale use for air separation was to produce nitrogen in the high pressure ammonia synthesis, a development which might be termed to have thrived between 1915 and 1925.

During this period the use of oxygen for welding was growing and, of course, has continued to the present. Something more than 900 separate plants for nitrogen and/or oxygen manufacture have been built by the Linde Company from 1903 to the present.

The field of application of oxygen for process purposes has been materially expanded by the development of the so-called Linde-Frankl process. The fundamental difference between this process and the older Linde method of manufacturing nitrogen and oxygen is that regenerators rather than tubular exchangers are used to reduce the energy requirement for the air liquefaction process. The change simplifies and cheapens the production of moderately pure oxygen (e.g. 98%) to an extent not likely to be fully appreciated without detailed study. The process, however, is not usable alone, for the production of a higher purity oxygen than 98%, for reasons which will become apparent later.

0. ORIGINAL PROCESS. - LINDE COMPANY

For completeness the reader is reminded that the original Linde process for liquefaction of air depends on the so-called Joule-Thompson effect, whereby air under high pressure when throttled through a valve will show a temperature reduction. The amount of temperature reduction with an adiabatic system is a function of initial temperature as well as pressure.^{*} By arranging for continuous heat exchange between incoming high pressure air and outgoing air after throttling expansion, progressive decrease in absolute temperature can be effected until finally part of the outgoing air will be sufficiently cooled to precipitate as liquid phase.

Commercial application of the phenomena involves introduction of all practical means to -

- (1) prevent the entrance of heat from outside the apparatus;
- (2) effect heat exchange between streams circulating within the equipment;
- ~~(3) purify the air prior to processing so that~~
traces of disturbing impurities do not interfere with the continuous operation.

* The data for the phenomenon, said to be used by the I.G. Farben, are given in Fig. 9 herein. These data were not obtained during the Linde Co. visit, but were abstracted from unpublished(?) I.G. Farben reports.

The separation of the liquefied air, which is of course, a mixture of about 20 wt. per cent liquid oxygen, and 80 wt. per cent liquid nitrogen, is effected by continuous distillation. The separation does not differ in principle from ordinary continuous fractional distillation except as is dictated by the circumstance that the temperature of separation is some 200° C. below the general surroundings. It is well known, of course, that the thermodynamic efficiency of a process is improved if small temperature differences only are caused to exist when heat exchange or conversion is involved. Usually, however, the investment required to obtain such conditions is not justified. In the liquid air field, however, the operating costs involved in attaining the low temperature level required, justify the large capital expenditure, so that the above mentioned principle is demonstrated on larger scale in this field, perhaps, than in any other field of commercial manufacture.

In describing the original Linde process above, compression of all the air to the highest required pressure was contemplated. It was pointed out long ago, however, by Lackman that the requirements of the distillation separation of air were such that only part of the air need be compressed to a high pressure and expanded. The rest of the air can be compressed to moderate pressures and cooled by heat exchange to a low temperature and then directly introduced into the fractionation equipment. Due to the low pressure drop characteristic of Frankl heat regenerators, the Linde-Frankl process can make use of this fact very effectively as will be later indicated, so that only a small portion of the total air liquefied is compressed to high pressure.

D. THE LINDE-FRANKL PROCESS - DESCRIPTION

The Frankl regenerators utilize the well-known principle of exchanging heat between gas streams by alternately heating and cooling solids packed in a tower through passage first of one gas and then the other through the packing. Four regenerators are used in the Linde-Frankl process--two on the cold nitrogen and two on the cold oxygen gas--as these gases emerge separately from the process equipment. Each of the regenerators is in turn used to cool incoming air at a pressure of about 4.5 Atmos. gauge. The timing of the cycle is adjusted with reference to the volume of the regenerators and the mass of packing material such that the temperature fluctuations at the upper and lower ends of the regenerators or "accumulators" are not too great.

The packing which has proved best for the accumulators, both from the standpoint of heat storage and also from the requirement of low pressure drop, is that proposed by Frankl. It consists of porous "pancakes" about one inch thick and of such diameter as to fit closely within the regenerator vessel. In making up such pancakes, two 1-inch strips of aluminum sheet each with corrugations or ruffles at an angle of 45° to the center line are laid together so that the corrugations are at right angles. The strips are thus held apart about $1/8$ " except at a series of points where they touch at the top of the corrugations. When the "strip pair" is wound up into a 1-inch flat spiral, the above mentioned circular pancake is formed and is thereafter held together by clamping wires. Figure 1a will make the construction clear. In packing the regenerator shell, a series of these pancakes is inserted, each laid flat on the one next below, until the regenerator vessel is finally filled as required. The assembly of the porous pancakes is such that a myriad of gas channels is presented for gas flow in the direction of the axis of the chamber. Altogether it is possible to arrange matters so that more than 1,000 square meters of heat exchange surface is presented by one cubic meter of the assembled packing.

Before describing the process for producing 98 to 99% oxygen, it should be stated that a number of different designs have been and are used according to the size of plant, cost of power, and needs of a specific installation. This description is based on the accompanying flow sheet, Fig. 1, stated by the Linde Company to be one of the more useful of the several variations of the process. Other schemes of operation using Frankl regenerators will probably be clear, once the principle of use in the following case is understood.

Referring now to the flow sheet (Fig. 1), the following describes the operations after the equipment is in temperature equilibrium. The turbo compressor shown at the lower right compresses all of the air which is to be processed, to about 4.6 atmos. gauge, after which the ~~stream is cooled indirectly by the adjacent water-cooled surface.~~ About 95% of this compressed and cooled air is then led through the cold accumulators of Frankl design. The cooling in the Frankl accumulator precipitates water vapor and carbon dioxide on the extended packing surfaces and the air finally reaches liquefaction temperature before passing out and into the bottom of the pressure fractionating column, (1), operating at about 4.4 atmos. gauge. Liquid containing about 39% oxygen is drawn off from the base of this fractionating column

and sent under its own pressure through a filter, (2), to remove traces of ice and/or solid carbon dioxide. The filtered liquid then passes to a point in the upper fractionating column where the mixture composition corresponds to that mentioned above.

The upper column operates at about 0.2 atmos. above normal pressure and separates the feed liquid by nitrogen reflux at the top into "pure" gaseous nitrogen at the top and "pure" liquid oxygen at the bottom. (NB-- Boiling points at atmospheric pressure are as follows: Nitrogen = -195.8°C ; Oxygen = -183.0°C).

The heat for fractionation in the low pressure (upper) column comes from the condensation of gaseous nitrogen rising to the top of the pressure column directly below. The tubular heat exchanger at the base of the upper column, and integral with the top of the lower column, thus has a double purpose. It supplies the heat for fractionation in the upper column and furnishes the reflux nitrogen liquid for the lower column, the heat exchange being made possible because of the "inversion" of temperature caused by the pressures chosen for the two columns. Part of the condensed nitrogen liquid at the top of the lower column, where it serves as reflux and is in turn flash vaporized to form the above-mentioned pure gas product. This nitrogen gas leaves the system by way of the Frankl regenerator assigned to nitrogen service at a temperature only 3° - 4°C below surrounding temperature.

The boiling liquid at the base of the upper column is substantially pure oxygen, and the proper proportion of the gas rising therefrom is deflected as oxygen product through the corresponding one of the Frankl regenerators. It emerges from the Frankl as the product stream of oxygen and at only 3 or 4°C below atmospheric temperature.

Each of the product streams, i.e., the "pure" nitrogen and the "pure" oxygen, remove by evaporation from the corresponding Frankl regenerator, the ice and solid carbon dioxide left from cooling of the incoming air in the previous phase of their operation. Thus each of the Frankl regenerators is not only again reduced in temperature, but is also put in a clean condition for good heat transfer, as well as for the further removal of water vapor and carbon dioxide from air led through in the next succeeding cycle. The evaporation of solids is complete enough so that, ideally, there is no need ever to remove the precipitated components by allowing the Frankls to

warm up. In actual practice, it often happens that several months elapse between such cleaning periods.

It should be noted, however, that the purity of both the oxygen and the nitrogen is somewhat impaired by the evaporation of the solids just mentioned, and also by the addition of the inevitable residue of air which is left in the regenerators after the air cooling part of the cyclic operation. Both sources of impurity are reduced in part by venting the pressure air before introducing the cold product streams, and sometimes by further venting the initial "pure" products, either wasting them entirely, or under certain conditions, passing them back to the process. It is obvious that many combinations of factors, such as cost of operation, relative value of higher vs. lower purity gases, undesirability of introducing too much water and carbon dioxide back into the system, etc., find interplay, together with the prejudice of operators, to effect many variations in actual practice at this point. In any case, however, the cycle is under the action of controllers, and when once manually set up proceeds with intermittent attention of the operators only. It is, however, quite impossible by any variation of the details of operation to attain the highest purity of products when the Frankl regenerator system is used as described.

It should be emphasized, however, that one of the important advantages of the Linde-Frankl scheme is directly connected with the disadvantage in respect to purity of products just mentioned. The offsetting advantage is that the inlet air to the process (with the exception of a small proportion to be presently mentioned) does not need to be scrubbed free of carbon dioxide and water vapor, such as is invariably necessary to prevent fouling stoppages when the older tubular type heat exchange is employed. A second advantage accrues from the very low pressure drop which can be secured with the Frankl regenerators in comparison to tubular exchangers effecting the same heat exchange at small temperature differences. Thus with the Frankl equipment it is not necessary to compress the gas initially to as high an intermediate pressure before cooling and introducing it to the fractionating column as would be the case if tubular exchangers were used.

It will be apparent that the process as described up to this point does not provide for the actual low temperature cooling required to overcome losses and inefficiency in operations. This is obtained by high pressure air liquefaction as follows: A relatively small high pressure compressor (extreme lower left of

the flow diagram, Fig. 1, takes suction on the cooled product from the after-cooler of the turbine air compressor and deflects to itself some 4.5% of this 4.6 Atmos. pressure air after drawing it through an alkali washer to remove carbon dioxide and most of the water vapor. The purified air is then compressed to about 180 Atmos. and thereafter is first water cooled and then cooled indirectly by ammonia refrigeration. (NB--The ammonia system is entirely separate from the rest of the equipment.) The refrigerated air passes through to two interchangers, Nos. 5 and 6, which together cool it to such a temperature that, after expansion, into a point near the middle of the upper (low pressure) fractionating column, it liquefies completely.

The low temperature cooling fluid for exchangers 5 and 6 is part of the liquid nitrogen from the top of the pressure column drawn through leveling pot 3. This liquid nitrogen, amounting to some 15% of the total weight of air being processed, is gasified and slightly superheated in passage through exchanger 6, after which it is expanded--without condensation--in the small expansion turbine (at the extreme right and middle of the diagram). Expansion is from the 4.3 - 4.2 Atmos. gauge, maintained in the lower column, to the 0.2 - 0.15 Atmos., gauge, employed in the upper column. The expanded nitrogen, recooled by the process of the expansion itself, passes through tubular exchanger 5 and to the atmosphere--or, more usually, is combined with cold nitrogen going to the Frankl. It may, however, be taken as a small stream of pure nitrogen product.

It must be noted that the necessity for removal of carbon dioxide prior to high pressure compression of the small stream of gas just described is due to the fact that tubular exchangers, 5 and 6, must be used in place of Frankl. regenerators. This is necessary since the heat exchange is between gases on the one side having a pressure of some 180 Atmos. and streams of nitrogen on the other side at substantially atmospheric pressure.

Typical quantities and temperatures may be given to amplify the above description. Figures were obtained from Dr. Richard Linde. All volumes are expressed in cubic meters, reduced to 760 mm. Hg. and 0° C. The unit of time is one hour.

Total Air Processed	11,900 m ³	comp. to 4.6 At
	765 m ³	" " 180 At
	12,665 m ³	

	<u>Nitrogen</u> Frankls	<u>Oxygen</u> Frankls
Low Press. Air m ³	9190 (2250
Cold Nitrogen m ³	9530 (
Cold Oxygen m ³	(2335

Total product Oxygen is as given for "cold" oxygen. Sum of oxygen and nitrogen produced is 12,235 m³, shrinkage from volume of total air processed is due to purging and losses.

Typical temperatures as follows:

Air into unit \neq 15° C.
 Combined air from both Frankls -172° C.
 (Nitrogen into Frankl, 1 & 2, -175° C.
 Oxygen into Frankl, 3 & 4, -172° C.

Both "pure" streams out of Frankls at about \neq 13° C.

Typical Column conditions would involve:

	<u>Lower Column</u>	<u>Upper Column</u>
(1) Pressure	4.2 At. Gauge	0.2 At. Gauge
(2) Temp. °C. Top	-182	-194
Bottom	-172	-185
(3) Reflux Liquid	Not directly given	3900 m ³ (Liq. N ₂)
(4) Product ^m Top	705 m ³ N ₂ (Liq.)	9530 m ³ N ₂ (gas)
Bottom	6900 m ³ (Liq. Mix)	2432 m ³ (Liq. O ₂)
(5) Plates	24	36
(6) Plate Spacing	90 mm.	90 mm.

* NB Amounts expressed as gas.

E. THE NUMBER AND LOCATION OF LINDE-FRANKL PLANTS

Altogether nearly 100 Linde-Frankl plants have been ordered but about 25 of these were canceled due to cir-

cumstances connected with the war. The tally, as we understood it, is therefore about as follows for the actual construction of Linde-Frankl plants:

Outside Germany, 7 plants, as given below.

Inside Germany, or occupied territories, 69 plants.

The average size of the plants inside Germany was stated to be about 3,000 cubic meters per hour of 98% oxygen. The largest installation of all was said to be that at Brūx, Czechoslovakia, where 10 units, each of 3,300 m³/h, 98% oxygen capacity, existed--or existed before bombing. Incidentally, the present condition of the various installed plants either in Germany or elsewhere was not known by the Linde Company at the time of our visit. If the writer's observation of several German plants constitutes a typical sample, one might hazard the guess that most of the German plants have not been seriously harmed and can be relatively easily repaired.

We were informed that all of the plants installed outside of Germany or German-controlled territory are contained in the list given as Table 1 on the next page.

TABLE 1

Serial No. of Plant	Ordered	Company Placing Order	Place of Installation	Production - m ³ /h	Purity (% O ₂)
5	1932	Panstwowa Fabryka Zwiaskow Azotowych w Mosciech, Moscice	Moscice (Poland)	500 O ₂	98
17	1936	I.G. Farbenindustrie A.G., Ludwigshafen (Contractor)	Nippon-Tar (Japan)	2250 O ₂	98
18	1936	Rep. of U.S.S.R. in Germany, Berlin	Leningrad	3500 O ₂	98
19	1936	" " " " " "	Leningrad	3500 O ₂	98
24	1936	Vereinigte Glühlampen- u. Elektrizitäts-A.G., Ujpest, (Krypton-Producing Plant)	Ajka (Hungary)	25000 (Air Processed)	-
31	1937	Bamag-Meguinn A.G., Berlin, 3. Contractor	Irvine (Scotland)	930 O ₂	98
32	1937	Bamag-Meguinn A.G., Berlin, 3. Contractor	Irvine (Scotland)	930 O ₂	98

F. COST OF OXYGEN FROM LINDE-FRANKL PLANTS

No very usable cost figures for oxygen manufactured by Linde-Frankl plants could be obtained during our visit, but the following data, given in a conversation, were said to be typical:

Electric power requirement is about 0.5 kw/nm³ of 98% O₂ produced. If electric power costs 1.5 pfg./kw. hr., the total cost of 98% oxygen was said to be distributed as follows:

Electric power = 50%
Amortization
and interest = 40% (Interest being taken at
5% on investment)
Other costs of
operating labor=10%

The above cost allocation was said to be sound for German conditions in the case of plants producing 2,000 m³/hr. oxygen or more.

Despite the almost irresistible temptation to translate these figures into dollars, it seems very doubtful if it is the part of wisdom to do so. In the writer's opinion, one should recognize an impossibility for what it is. The chief interest in obtaining a dollar cost figure is to determine what might be expected from some plant subsequently built. German labor conditions, manufacturing conditions, and all other items going into investment and power costs will doubtless be so changed that sound assumptions cannot be made at the present moment. So far as past conditions are concerned, the Dollar equivalent of the Mark comes into question. The less one is familiar with the background of German pre-war and war economics, the more ready he is to assign a dollar equivalent to the Mark under the Nazi regime. With full realization of the unsatisfactory condition which remains when leaving this discussion as at present, the writer prefers not to translate cost figures any further than may be implied by the single statement that the power requirement typical of the larger size Linde plants is about 0.5 kw/nm³ of 98% oxygen produced.

Table 2, below, gives some detailed power consumption figures for Linde-Frankl plants as a function of the purity of the oxygen mixture produced. These figures include all the power required for an operating unit and the two rows of figures at the bottom of the table show corresponding figures for two of the higher purities when tubular exchangers are used in place of

Linde-Frankl regenerators. It should be noted that the last column of the table shows that it is more convenient to speak of power costs in terms of cubic meters of nitrogen removed in order to make the various mixtures. In going from 40% oxygen to 98% oxygen, it will be noted that the power consumed per m³ of nitrogen removed, increases a little more than 25%.

Table 2

Power Consumption Figures for the Production of
Oxygen of Various Purities

Purity of the produced Oxygen Mix- ture	Power Con- sumption per m ³ Oxygen Mixture	Power Con- sumption per m ³ pure Oxygen Mixture	Volume of Nitrogen to be re- moved from the air per m ³ Oxygen Mixture	Power Con- sumption per m ³ Removed Nitrogen
% O ₂	KWH/m ³	KWH/m ³	m ³ /m ³	KWH/m ³
40	0.09	0.22	0.92	0.095
60	0.19	0.315	1.87	0.1
80	0.31	0.39	2.83	0.11
90	0.38	0.425	3.31	0.115
98	0.445	0.455	3.69	0.12

To be compared with the figures for a large plant utilizing tubular exchangers:

98	0.65	0.665	3.69	0.175
99.7	0.73	0.73	3.77	0.195

G. MISCELLANEOUS

The Linde Company was under the necessity which beset nearly all German manufacturers, before and during the war, namely, of conserving all special metals. Copper is the ideal material for low-temperature work and has always been used for the purpose. Dr. Richard Linde advised us that due to shortage of copper many steels were tried. ~~With all but one exception these proved unsatisfactory~~ for low-temperature operation. However, steel No. 445 of the German list of war steels was satisfactory, and or "Deutro TT-A 23," said by Dr. Linde to be a steel of composition:

Carbon	0.4%
Manganese	18%
Chromium	3 to 5%

It was not clear whether this steel was identical with No. 445 mentioned above or not, but reference to the German list of war steels--not available at present writing--may clear this point. "Deutro" steels were made by Deutsche Rohrenwerke A.G. (Düsseldorff, Ger.) but reference to a 1937 Catalogue shows no listing as Deutro TT-A23.

Dr. Linde was quite specific to the effect that the preferred material for low temperature work was copper and that in spite of its higher purchase cost fabrication was somewhat simpler and that in the end it was the cheapest material available for low-temperature work. Ordinary soft solder is entirely satisfactory for sealing copper joints as in tube sheets, and this procedure is of course much cheaper than any which can be used where steel is involved. Furthermore, drawn copper tubes of thin wall section are practical, whereas the tubes with equally thin wall cannot be obtained in any steel, particularly one of analysis such as the above, which cannot be classed as easy-working material.

H.

SEPARATION OF GASES OTHER THAN AIR BY LOW TEMPERATURE--LINDE PROCESSES

A short discussion of gas separation processes was also had with Dr. Linde, though the time available was so short as to give only fragmentary information. Furthermore, it was found that Dr. Linde himself was not particularly conversant with the details of these processes. Those of his engineers who were more conversant with the matter were not available during the afternoon visit.

J. HISTORY

It may be mentioned that the Linde Company first entered into the field of gas separation other than air in 1910--in order to make hydrogen, principally for fat hardening, from water gas. While a few plants of this character were built, the Bamag process for hydrogen production and also that of the I.G. rendered the Linde process of little commercial interest. The matter was only taken up again seriously in 1924, when Sennet-Solvay applied to Linde in 1924 for a plant to make hydrocarbon separation from gas which they expected to have available at their ammonia plant at Ostende, Belgium.

It is a fact that carbon monoxide is very soluble in liquid nitrogen, and plants using this method of removing carbon monoxide from hydrogen or other gases were manufactured in considerable numbers between the years of 1926 and 1931. This was the period in which low-temperature plants to manufacture hydrogen and nitrogen in the proper ratio for ammonia synthesis thrived. There were said to

be some 200 units of this character in operation.

K. HYDROGEN-NITROGEN, FOR AMMONIA PRODUCTION

Figure 2 shows the over-all features of a plant to process gas from coke ovens and make a principal product gas suitable for ammonia manufacture. The rectangle at the upper righthand corner of Figure 2 is shown in detail on Figure 2-a. It is outside the scope of this report to go into detail as to this operation, but it is believed the main features will be apparent by a study of the diagram.

Briefly, coke oven gas is compressed, benzole is separated, and carbon dioxide is washed out first by water and then by suitable alkali solution. Precooling of the washed product is accomplished by an ammonia cooling system and the purified cooled coke oven gas then passes to the low temperature equipment shown on Figure 2-a. Heat exchange with outgoing products cools the material to precipitate out methane as liquid and the carbon monoxide is washed out of the gas by liquefied nitrogen, liquefaction being carried out by the well-known Linde method, making use of the Joule-Thompson effect. The liquefied products, including liquefied methane and ethylene, also the liquid stream of carbon monoxide dissolved in nitrogen, pass out of the equipment after exchanging "cold" with the incoming materials. A somewhat different version of the low temperature part of a unit to make the raw material for ammonia synthesis is shown in Figures 3 and 3-a. Its operation will be clear on following the flows shown in the diagrams.

Figure 4 is a partial diagram and Figure 5 is a complete flow diagram of equipment which the Linde Company installed in Japan. The equipment of the installation given by Figure 5 consisted of two aggregates for nitrogen manufacture at the rate of 1,500 cubic meters per hour and two gas aggregates each 5,000 cubic meters per hour of a mixture of hydrogen and nitrogen. Here again a complete discussion of the diagrams is outside the scope of this report, but it is believed that those acquainted with the art will find little difficulty in following the flows.

In recent years the Linde Company has been called upon to manufacture numerous plants for the separation of hydrocarbon gases by low temperatures. As in the case of the low temperature equipment shown in Figure 6 the purpose was to produce pure methane by separation of coke oven gas as well as the separation of "converted" water gas.

While it is not intended to fully detail conditions maintained in the equipment of Figure 6, it may be mentioned that the coke oven gas entering at the upper left of the diagram was under a pressure of 12 At. and at -40°C by reason of precooling in an ammonia cooled installation which is not shown. The complicated exchanger system indicated by items 1, 2 and 3 effects precipitation of ethylene and also of liquid methane which is distilled in column 4 and taken as a pure stream at the upper lefthand corner of the page. The gas, substantially free of methane, passes from separator 10 into the wash column 6, such entering gas having a composition of about 8% nitrogen and 88% hydrogen, together with 4% CO which is to be washed with nitrogen in this low temperature apparatus.

Liquid nitrogen is prepared by high pressure compression of nitrogen not shown except as the incoming high pressure line at the upper righthand corner of the diagram. Exchangers 11, 12, 13 and 14 bring this nitrogen to low temperature with the assistance of exchanger 8, which is just before the expansion valve where the Joule-Thompson effect causes liquid nitrogen to precipitate and form the wash liquid for column 6. The mixture of nitrogen and nitrogen freed from carbon monoxide by this washing then passes out through heat exchangers 3, 2 and 1 in series to make a suitable raw material for ammonia synthesis. The pure methane stream has already been discussed and other streams which may be taken from the unit will be apparent from a study of the diagram.

The apparatus just described for the production of pure methane involves the use of nitrogen as refrigerant but may be said to constitute the link between the older avenue of effort of the Linde Company and a newer field, namely, the separation of pure components from mixtures of light hydrocarbon gases. Figures 7 and 8 show two designs for the recovery of ethylene from its admixture with higher and lower boiling hydrocarbons.

L. SEPARATION OF HYDROCARBON MIXTURES

Figure 7 shows a design for separating hydrocarbons which does not use liquid ethylene as a circulation stream for low temperature cooling. The reader will probably find no difficulty in following the flows in the diagram, but it may be mentioned that after compressing the crude gas in Compressor 1 and precooling it with ammonia refrigeration (not shown), propane is separated out with fractionation at the base of column 8. Reflux is maintained by ammonia. The gas then passes to additional cooling by an evaporating mixture of C_2 constituents, then is used as a reboiler stream at the base of column 9.

It is filtered free of ice and other solids, and then finds its way into the middle of column 9. Fractionation occurs under the action of liquid methane reflux to produce a mixture of C_2 compounds at the base and pure methane at the top. This mixture is vaporized by exchanger 12 and passes to column 10, where it is fractionated to a bottom stream of liquid ethane and a top product of liquid ethylene.

Liquid ethylene for refluxing column 10 is obtained by a circulation stream with the aid of compressor No. 3, which, however, only compresses the ethylene to about 4 Ats. Methane reflux to column 9 is also obtained by recirculation through compressor 2, which compresses same to about 40 Ats. Both the ethylene and methane are precooled by exchangers shown in the diagram before the expansion and liquefaction stage just prior to entrance into the top of their respective columns.

Figure 8 shows similar processing of a hydrocarbon gas containing all constituents up to and through the C_3 fraction, together with a trace of C_4 . The scheme can be easily followed in the diagram, which is more detailed than Figure 7, especially in that the pressures in all the columns and at various other parts in the apparatus are indicated. Referring to the diagram, note that the compressor at the lower lefthand corner compresses the crude gas from one At. and normal temperatures in three stages to 30 At. gauge, after which it is ammonia cooled in A24 and then passes (through filters) into column 1, where propane reflux is furnished at the top by ammonia coils and where outside heat furnishes the energy for reboiling the bottoms.

The depropanized overhead passes to column III which takes all methane overhead and a mixture of C_2 s at the bottom. Cooling for reflux at the top is obtained by boiling a fractionated mixture of ethylene at about 1 At. pressure, the vapor being the ultimate ethylene product from the plant. Reboiling at the bottom is obtained from an ethylene stream which has been dried but not cooled after compression from a fraction of an atmosphere to 40 Atms.

The bottom mixture of C_2 s is expanded in heat, but not material, exchange, with the vapors of methane rising from the column III and the heat of vaporization so picked up allows the mixed feed to column IV

to be in the gas phase. Column IV separates the mixture into ethylene (top) and ethane (bottom). The gaseous overhead of substantially pure ethylene at 0.2 Atm. is warmed by heat exchange and then passes to a four stage piston compressor which compresses part of it to 40 Atm. The path of the 40 Atm. material is (a) through drier, (b) through Column III reboiler as aforementioned, (c) through ammonia coolers, (d) through filter and then to expansion for cooling in the top of Column III, after which it leaves equipment through exchangers as product ethylene. The portion of the ethylene which is compressed to only 4 Atm. is withdrawn from the 2nd stage of the compressor, is filtered, then passes inside the reboiler tubes of column IV, and is then expanded to form reflux ethylene for column IV.

From the pressure conditions one may surmise the column conditions to be somewhat as follows:

	<u>Col. I</u>	<u>Col. III</u>	<u>Col. IV</u>
Pressure (gauge)	30 Atm.	(28-29 Atm) (1)	0.2 Atm.
Temperature Top (°C)	-	- 104	- 127
Bottom (°C)	83-86	About 0 depending on constitution of mixture.	- 109

Note (1): Pressure is estimated only on basis that boiling (product) ethylene, probably at only slightly above 1 Atm., is used to condense methane together with fact that there would seem to be no reason to reduce pressure from column I other than by a small amount for independence in control of column III.

The interested reader with facilities and data for heat balances at hand may proceed to make better estimates of column conditions than the above table represents. Temperatures were in all cases estimates from a very crude Cox chart. No information other than that on flow sheet was available to present report writer, who was handicapped by lack of fundamental data and/or time and facilities to accumulate them from library research.

M. CONCLUSIONS

It is a source of regret to the writer of this report that circumstances did not permit the expenditure of at least a full day's additional time to accumulate more detailed and exact information on the

methods

separation of hydrocarbon gases by Linde. Other groups had the opportunity of spending a much greater length of time at this location, and their reports will no doubt be much more detailed. It seems apparent, however, that the Linde designs do not involve any procedures which are actually novel in the sense that they embody any new principles or procedures which would not occur to those acquainted with the art. The distinguishing feature of the design of Linde plants in general is that heat recovery is practised to a very extended degree. Under other manufacturing conditions and with other rates of amortization of investment, labor and power costs for the operating plant, it may well be that smaller heat recovery is economical, even at the expense of greater power cost. Dr. Richard Linde stated that the theoretical minimum requirement to separate nitrogen and oxygen from air (both - presumably(?) - 99.5% pure) was 0.2 Kw hr per nm³. It will be noted from Table I that this minimum is only exceeded some 2.5 times in large plants, and Dr. Linde was of the opinion that any significant improvement in efficiency was unlikely so far as air separation plants were concerned.

The Linde Company has perhaps had more extended experience than any other in the field of commercial plant design for very low temperatures and their findings, as exemplified by unit designs, warrant thorough and extensive study, and all the more so, since different economic conditions in the future in Germany and elsewhere, will doubtless mean that older designs need modification even though, possibly, they were of the soundest, when initiated.

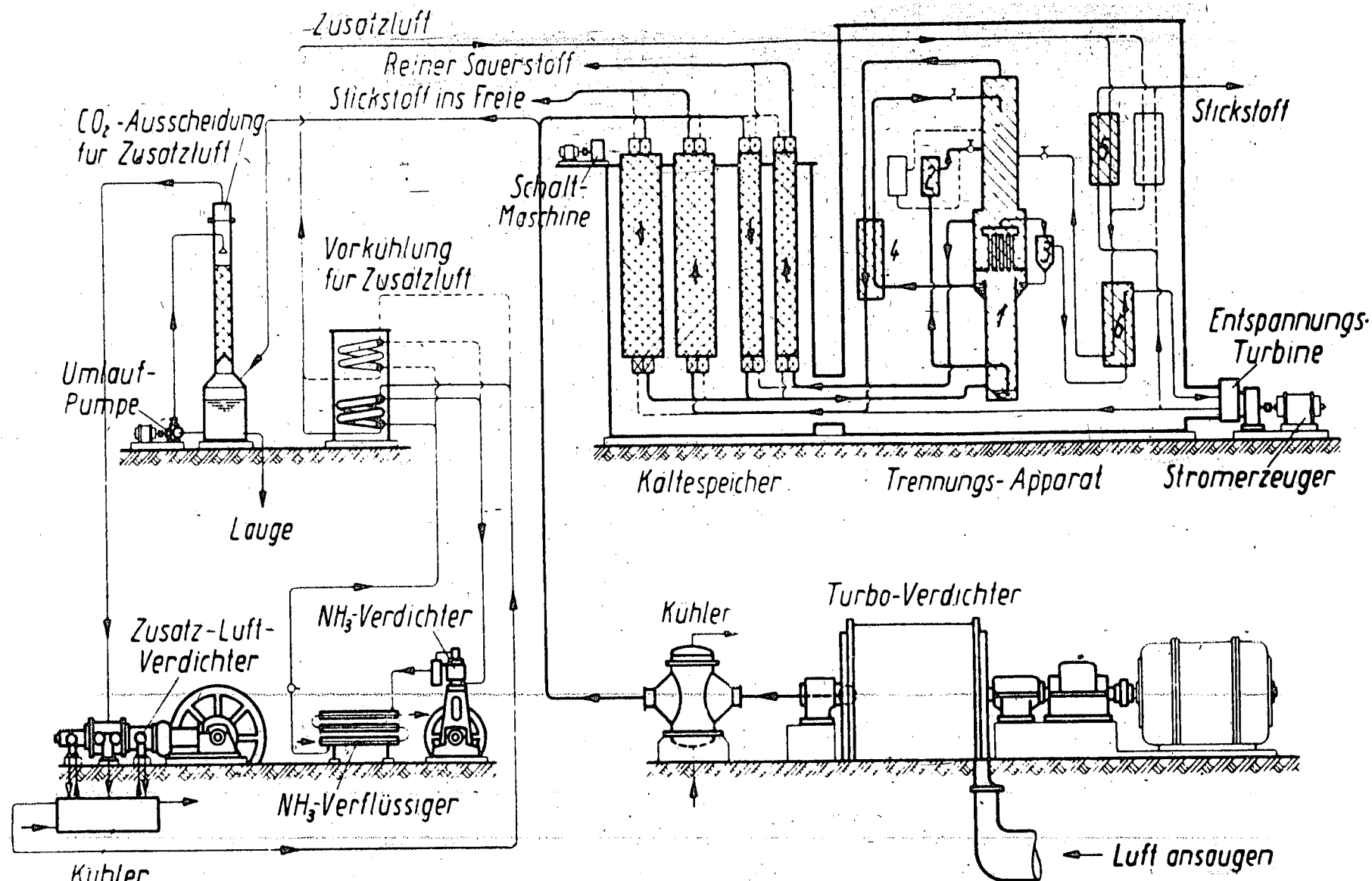


Fig. 1 Flow sheet of a Linde-Frankl Plant for the production of oxygen of 98%.

1 = Rectification columns / 2 = Filtre for purification of the liquid oxygen coming from the 1st column

3 = Separating vessel / 4, 5 and 6 = Counter-current interchanger.

Zusatzluft	Additional-Air	Lauge	Caustic Soda Lye	Entspannungs-	} Expansion
Reiner Sauerstoff	Pure Oxygen	Schaltmaschine	Reversing Engine	Turbine	
Stickstoff ins Freie	Nitrogen in the open	Kältespeicher	Cold Accumulator	Zusatz-Luft-	} Additional-
CO ₂ -Ausscheidung	CO ₂ -Absorption	Trennungs-	} Separating	Verdichter	
für Zusatzluft	} for additional-air	Apparat		NH ₃ -Verdichter	NH ₃ -Compressor
Vorkühlung für		} Electric Current-	} Generator	NH ₃ -Verflüssiger	NH ₃ -Liquefyer
Zusatzluft	} additional-air	Stromerzeuger		Turbo-Verdichter	Turbo-Compressor
Umlaufpumpe	Circulating Pump	Kühler	Cooler	Luft-Ansaugung	Air Intake

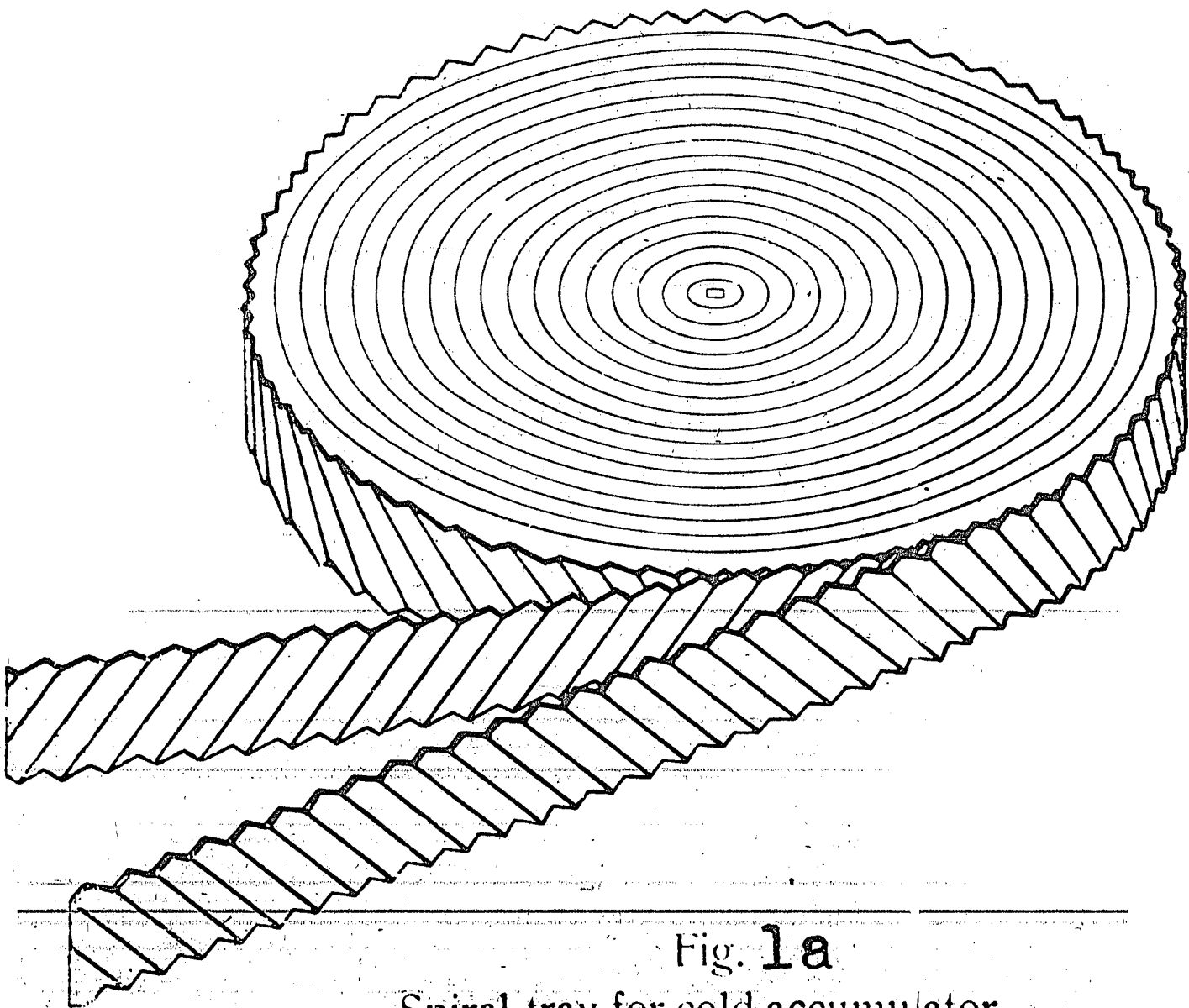
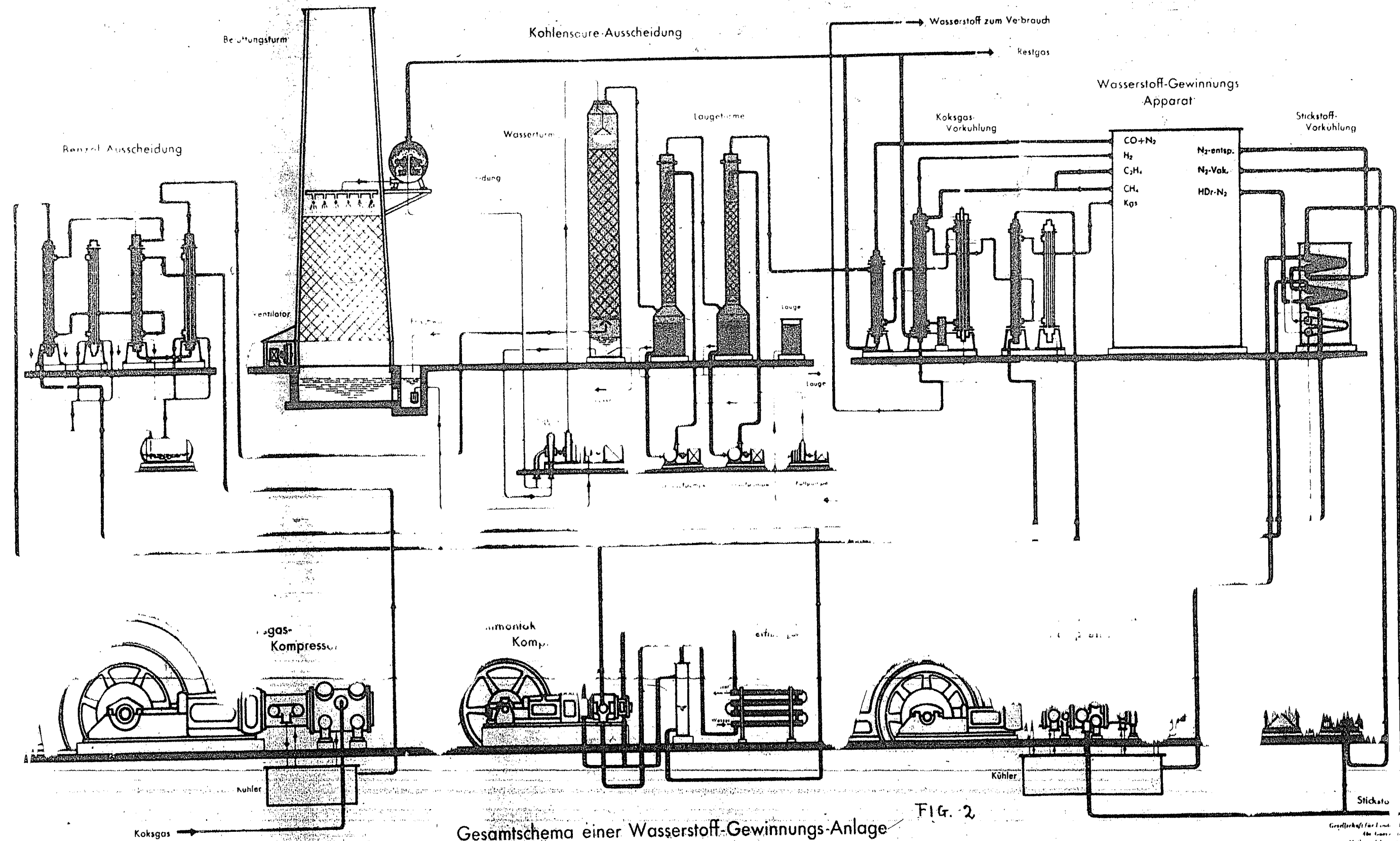


Fig. 1a

Spiral tray for cold accumulator.



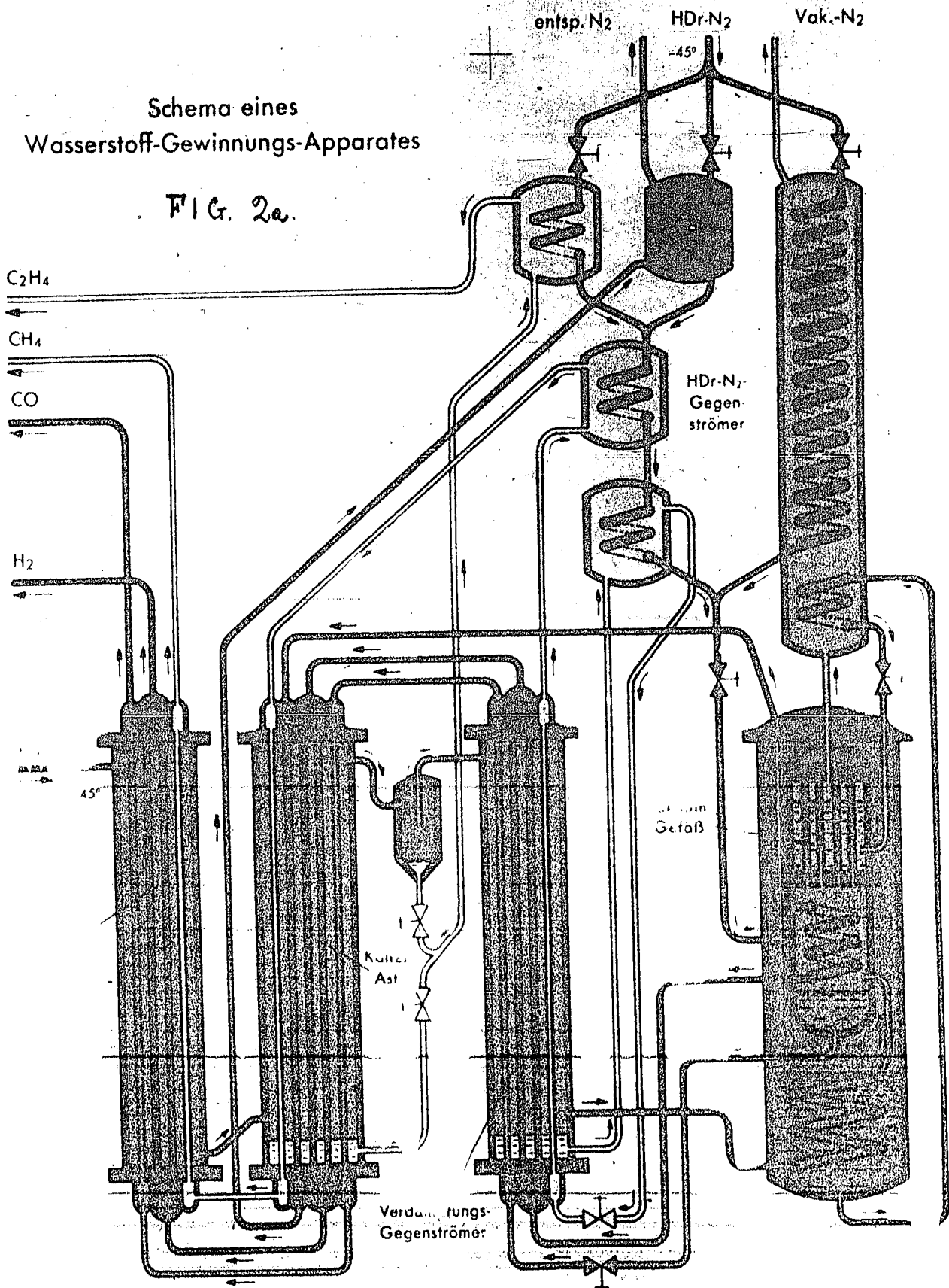
Gesamtschema einer Wasserstoff-Gewinnungs-Anlage

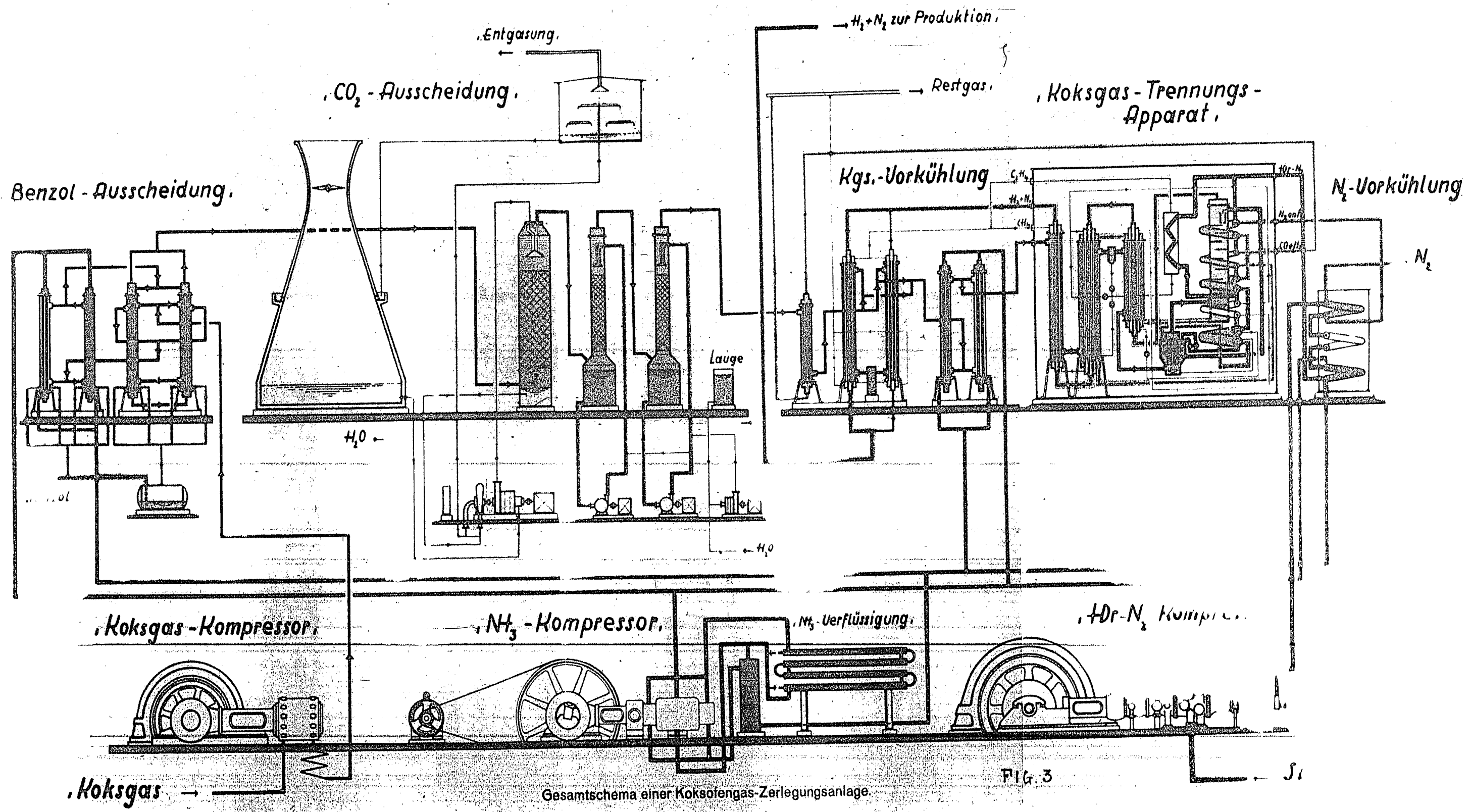
FIG. 2

Gesellschaft für Erdgas- und Wasserstoffgewinnung

Wasserstoff-Gewinnungs-Apparates

FIG. 2a.





Gesamtschema einer Koksofengas-Zerlegungsanlage.

Fig. 3

S.

FIG. 3a

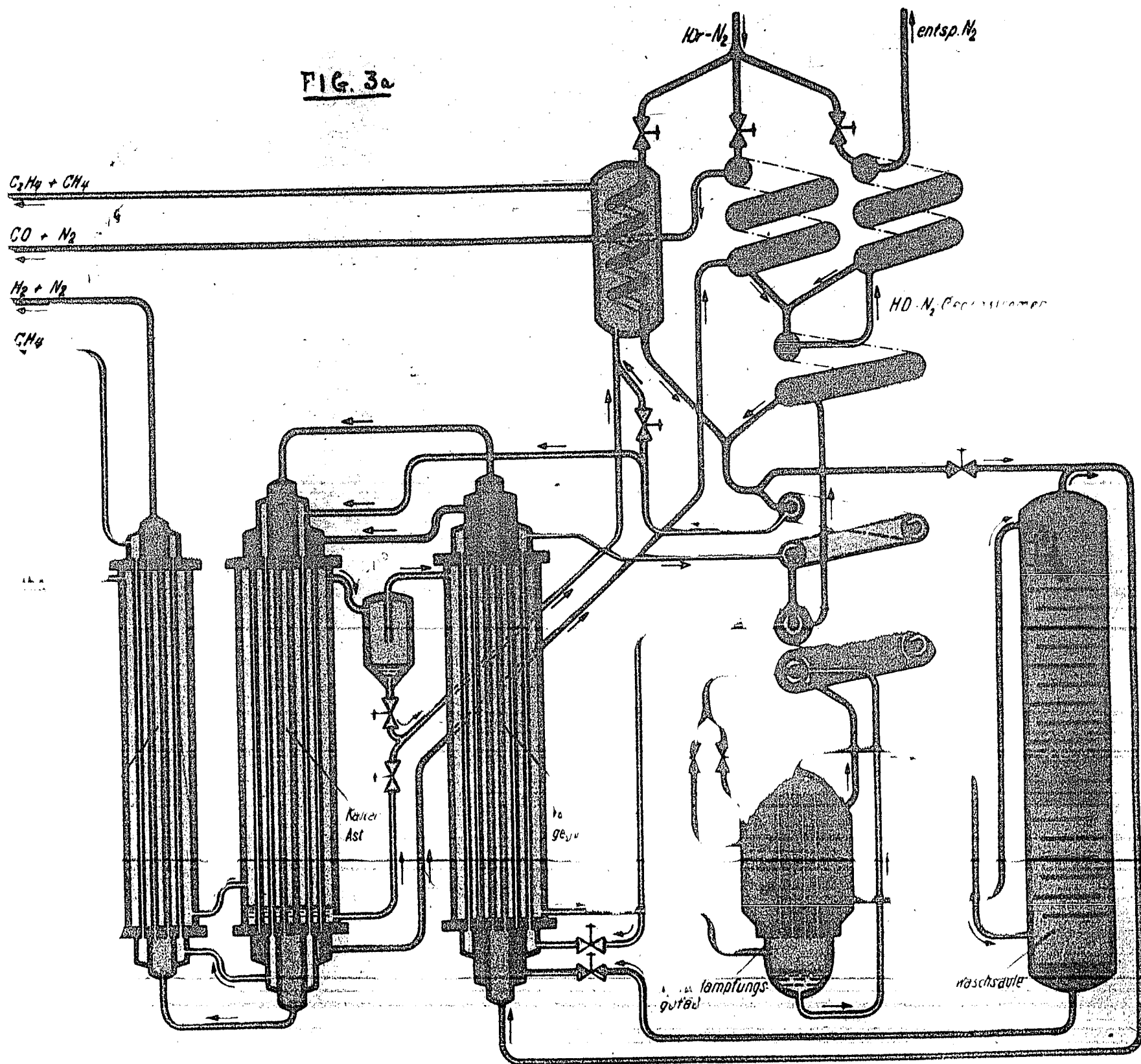
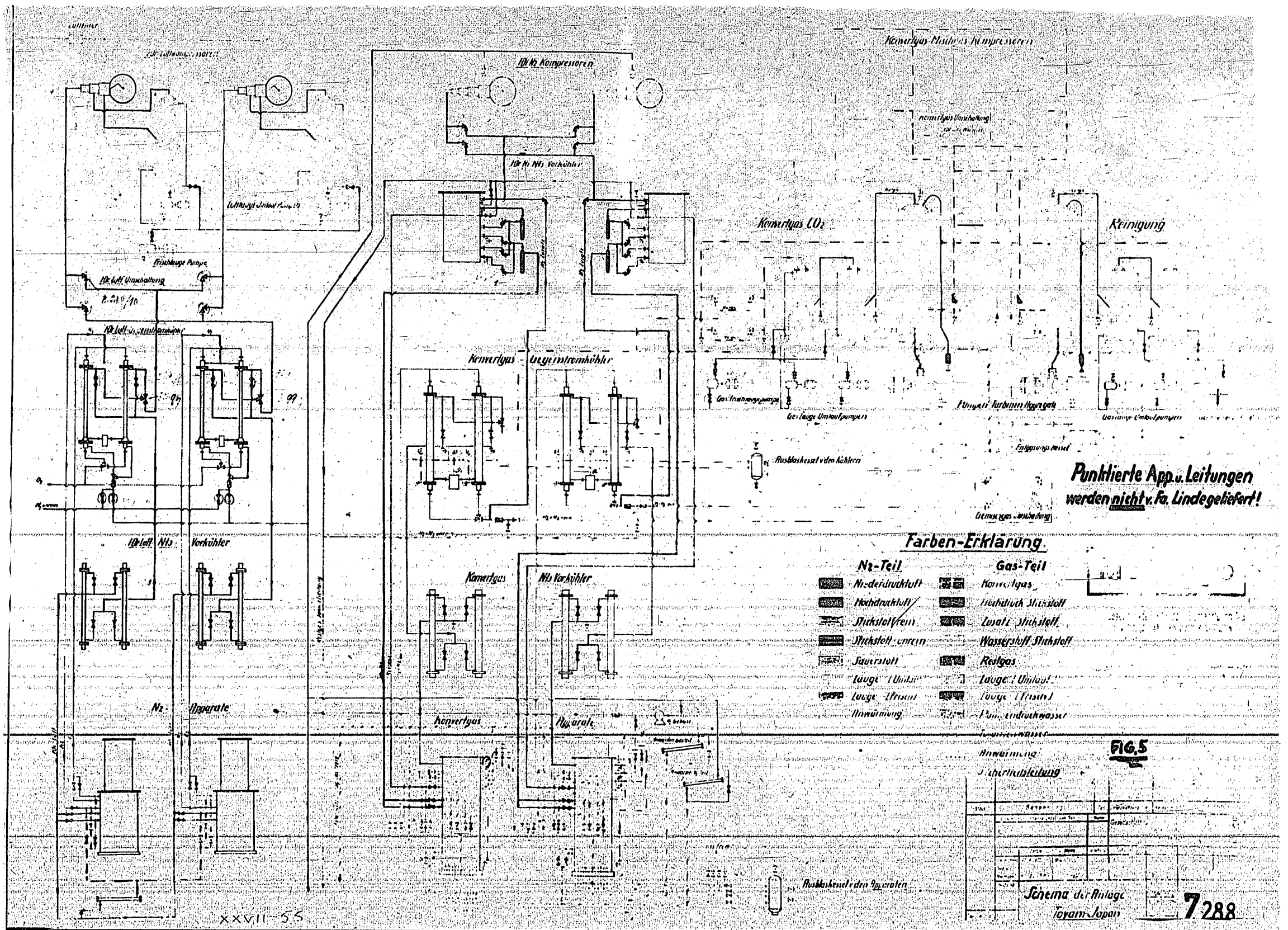
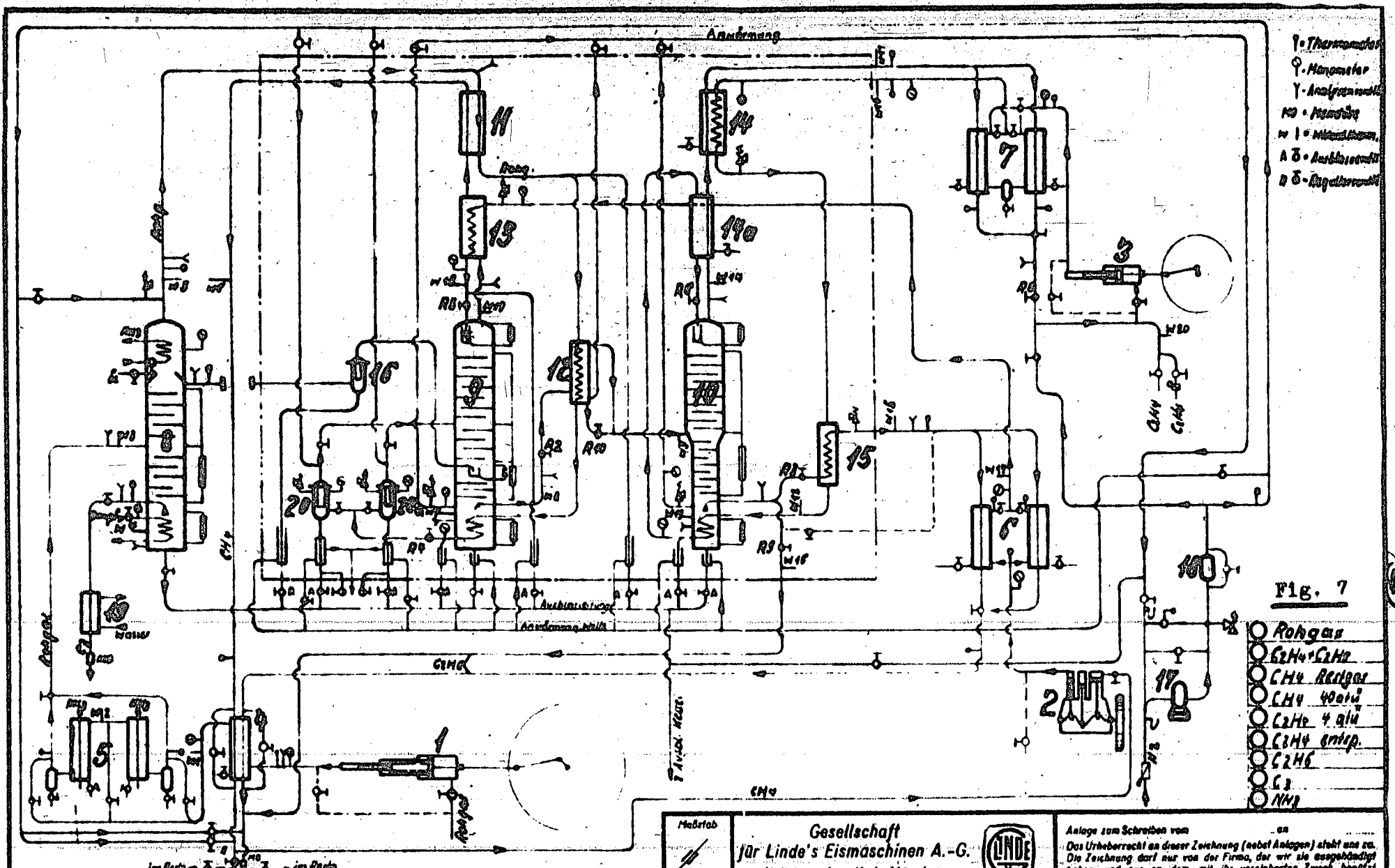


FIG. 4

<input type="checkbox"/> Festgas	1. Festgas	4. Neugegensprachen-Festgas	7. Dampfgegensprachen-Festgas
<input type="checkbox"/> Flüssigkeit	2. Verdampfungs-Gegegensprachen	5. Neugegensprachen-Flüssigkeit	8. Dampfgegensprachen-Flüssigkeit
<input type="checkbox"/> Dampf	3. Wasserdampf	6. Dampf-Verdampfungsgegegensprachen	





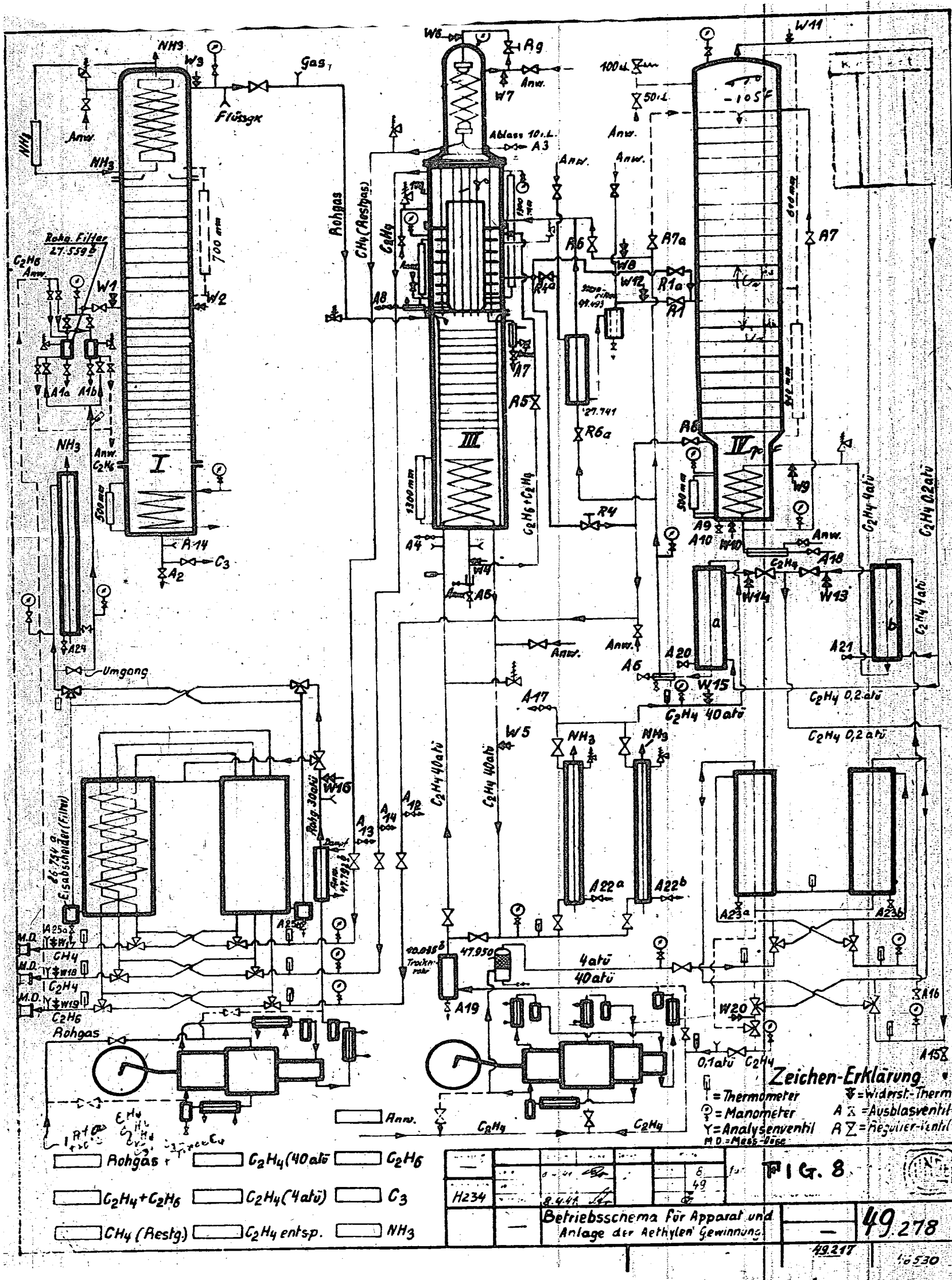
- Y - Thermometer
- Q - Manometer
- Y - Analysenrohr
- MS - Messung
- W 1 - Messung
- A B - Analysenrohr
- D B - Analysenrohr

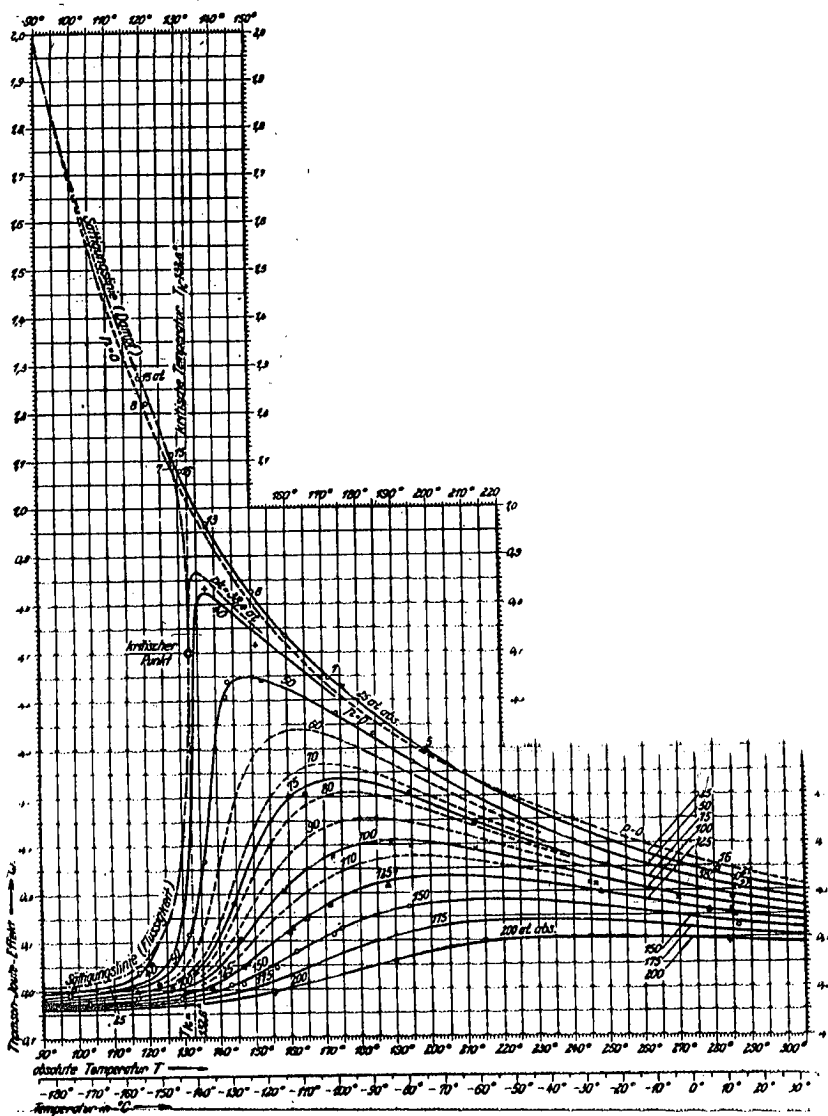
Fig. 7

- Rohgas
- C₂H₆ C₂H₄
- CH₄ Rohgas
- CH₄ 400 l/h
- C₂H₆ 4 q/h
- C₂H₄ 6 m/h
- C₂H₆
- C₂
- NH₃

1 Rohgas-Kompr.	8 C ₂ Säule	15 C ₂ H ₆ Verdampfer
2 CH ₄ Kompr.	9 CH ₄ Säule	16 Filter
3 C ₂ H ₆ Kompr.	10 C ₂ H ₆ Säule	17 Anndm.-Gebläse
4 Rohg. Gegenstr. Kühler	11 Rohgas. Gegenstr.	18 N ₂ Anndimer
5 Anndm. Vorwärmer	12 C ₂ Verdampfer Gegenstr.	19 C ₂ Nachwärmer
6 CH ₄ Gegenstr. Kühler	13 CH ₄ Verdampfer	20 Filter
7 C ₂ H ₆ Gegenstr. Kühler	14 C ₂ H ₆ Gegenstr.	21 Filter

Maßstab 1:1	Gesellschaft für Linde's Eismaschinen A.-G. Holtriegelskreuth b. München				Anlage zum Schreiben von	
	Das Urheberrecht an dieser Zeichnung (nebst Anlagen) steht aus zu. Die Zeichnung darf nur von der Firma, der wir sie ausgehändigt haben, und nur zu dem mit ihr vereinbarten Zweck benutzt werden. Soweit ein Zweck nicht besonders vereinbart ist, besteht der Zweck der Überlassung der Zeichnung lediglich darin, dem Empfänger den Betrieb der auf der Zeichnung dargestellten Ma- schinen, Apparate oder Einrichtungen zu erleichtern. Die Zeichnung ist vom Empfänger geheimzuhalten und auch so aufbewahrt werden, daß sie Unbefugten nicht zugänglich ist. Durch die Entgegennahme der Zeichnung erklärt sich der Emp- fänger mit den vorstehenden Bedingungen einverstanden.					
Werkstoff H 175	Datum 27.11.41	Name N	Genehmigt H	Körner	Fach X	Erster Einbau Erstellt durch <div style="border: 1px solid black; padding: 5px; font-size: 2em; float: right;">77245</div>
Kommission H 175	Gezeichnet 27.11.41	Normgepr. 28.11.41	Reg.	Gruppe	Reg.	
Schema einer Anlagen-Anlage ohne 10r-C ₂ H ₄ Kreislauf						Ersatz für Entstanden aus 7338





Differentialer Thomson-Joule-Effekt der Luft bei tiefen Temperaturen,
dargestellt durch Kurven konstanten Druckes in Abhängigkeit von der Temperatur
Versuchspunkte: ○ unter 25 at (die beigefügten Zahlen geben den Druck in at an),

✓ 25 at + 40 at □ 50 at × 100 at 125 at ○ 150 at 200 at

FIG. 9.