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THE INTERNATIONAL SERIES OF MONOGRAPHS ON PHYSICS

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BY

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PREFACE TO SECOND EDITION

THE scientific principles underlying the technique of gas separation have remained virtually the same over a number of years, but the technique itself has developed considerably. The necessities of war and the severing of old ties have led to the growth of independent thought in the fields of applied physics and chemical engineering in several countries, including our own. The separation of gases by distillation at low temperatures is no longer a foreign innovation but is rapidly becoming a recognized practice in Britain. Industrial firms, scientific laboratories, and university teachers are showing an increasing interest in the subject, and a number of commercial plants are now being designed and manufactured in this country.

Under these circumstances, a change is taking place in the demands on scientific and technical literature. In addition to a general introduction to the subject, which it was the original purpose of this book to present, a need has arisen for a more detailed technical treatise, addressed primarily to those engaged in the design and operation of low-temperature plants.

To have tried to meet such a demand within the framework of this volume would have necessitated a complete change in its character, and I did not feel that such a change was warranted. I have preferred to bring the contents reasonably up to date and to alter, and I think improve, the theoretical approach in certain chapters, while preserving, as far as possible, the original conception of a survey of the scientific and technical field. I trust that others will provide, in due course, the engineering text-books which the practical man requires.

I have somewhat altered the thermodynamic treatment of liquid and gaseous mixtures in Chapters II and IV with a view to making it more easily intelligible, and I have amplified the discussion on heat-exchangers and regenerators in Chapter III in order to facilitate an understanding of the problems facing the chemical engineer. In Chapter VI the analysis of air-separating plants from the point of view of irreversibility has been carried a stage farther than in the First Edition in view of the importance of power economy in modern large-scale oxygen plants. For the same reason considerable space has been allotted in Chapter VII to an examination of the Linde–Fränkl Process, and the more recent oxygen plants developed in various countries have been briefly discussed.

New features in the production of the rare gases are reviewed in Chapter IX and the separation of cracker gases has been somewhat extended in Chapter XII to cover designs put forward since the end of the war, in the United States and in this country. The growing importance of hydrocarbons has led me to rewrite Chapter XI and to devote considerable attention to their production from industrial gases based on coal as well as on oil.

I would like to acknowledge the advice and encouragement of numerous friends and colleagues, especially of the Management and Staff of Petrocarbon Ltd., and to thank my assistant, Mr. J. B. Axon, for his valuable help in many calculations.

M. R.

September, 1948

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INTRODUCTION

THE PRINCIPLE OF THERMODYNAMIC EQUILIBRIUM

ALL natural gases and all primary gaseous products of industrial processes are complicated mixtures containing a large number of chemical components in the most diverse proportions. In order that they may be put to economic use, it is often necessary to alter their compositions considerably. In many cases it is even profitable to separate gaseous mixtures into their pure chemical components. The processes used to bring about changes in the composition of gaseous mixtures, whether these changes lead to pure components or merely to products differing in composition from the original mixture, are known as gas separation.

Let us consider at first, for the sake of simplicity, a binary gaseous mixture which is to be separated into its pure components. We must conceive a continuous process such that an uninterrupted current of mixture enters the plant at one point and two currents of pure gas leave it at two other points. Somewhere in the interior of the apparatus the actual separation takes place, either in one step or in several steps, or else in an infinite number of infinitesimal changes of concentration.

For this to occur, the apparatus must contain certain surfaces on either side of which the mixture will have different concentrations. If separation is effected in one step, we shall need, in principle, two such surfaces; the mixture is introduced between them and on the outer side of each a pure gas is emitted. For separation in several steps we shall need more surfaces and, in the limiting case, an infinite number, across which infinitely small concentration heads will subsist. These surfaces cannot, of course, consist of impermeable walls, since interaction must occur between the substance on one side and that on the other. As we shall see, the surfaces need not contain any bodies apart from the mixtures that are being treated.

There are several kinds of surfaces across which differences of concentration may be brought about and maintained. But of these a certain group is much more important than the others, and this group alone will concern us here. The surfaces of this group are characterized by the fact that across them a certain finite concentration head automatically comes into being and maintains itself of its own accord for an unlimited period of time. These surfaces are the phase boundaries of a system in thermodynamic equilibrium.

According to the laws of thermodynamics, a system consisting of

several components in several phases is in equilibrium if the temperature, pressure, and chemical potential of each component are the same in every phase. Thermodynamics does not require that the concentrations of each component be the same in every phase. On the contrary, the chemical potentials of the several components will, in general, not be the same in the various phases unless the concentrations differ. Except at certain singular points, two phases containing more than one component, when in equilibrium with each other, will have different compositions. This is the fundamental physical law underlying all commercial methods of gas separation.

Now it is a well-known fact that a system in equilibrium can have but one gaseous phase, since all gases are completely miscible. On the other hand, in order that phase boundaries may exist, we must have at least two phases. Hence it follows that one of the phases concerned must be in a state other than gaseous. In order to separate a gaseous mixture by methods involving phase equilibrium, at least part of the gas must be transformed into a state of different aggregation. This may be attained in various ways:

1. *The gas may be partly liquefied.* This can be achieved only at temperatures below the critical. Since the critical temperatures of most gases are below room-temperature, this entails refrigeration. This leads us to the low-temperature method of gas separation, which is of by far the greatest importance and is the subject of this book.

2. *Part of the gas may be dissolved in a liquid solvent.* This is a very frequent method for removing impurities of low concentration. It should be noted that, as concerns thermodynamic equilibrium, it differs from the first only through the introduction of a fresh component.

3. *Part of the gas may be sorbed on a solid sorbent.* Here again we can achieve thermodynamic equilibrium between the free gas and the phase consisting of the sorbed gas and the sorbent. We have again merely introduced a new component, this time a solid.

4. *Part of the gas may be chemically bound to a solid or liquid substance or may undergo some chemical reaction associated with a change of phase.* As in this case the reacting part of the gaseous mixture usually undergoes permanent changes and thus ceases to exist as such, these 'chemical' methods are usually not included in the term gas separation. However, in principle, the laws of thermodynamic equilibrium are independent of whether chemical reactions do or do not occur in the system. This type should therefore be included in our list.

All the above-cited devices, however different they may appear at first

sight, are based on the same fundamental phenomenon: a separation into several phases in equilibrium involves coexisting mixtures of different composition on either side of surfaces, and thus brings about partial separation of the mixture. Since these concentration heads are independent of time, they can be made the basis of continuous processes.

One phase boundary will generally not lead to complete separation of the mixture but only to a slight change in composition. To separate a gas into its pure components, the process has to be repeated. This is the science of gas separation which we describe in subsequent chapters.

A few examples may serve to illustrate these arguments.

If atmospheric air, which we may here consider as a binary mixture, containing 79 per cent. of nitrogen and 21 per cent. of oxygen, be cooled to a temperature of $-193°$ C. at atmospheric pressure, it will separate nto a gas containing 87 per cent. of nitrogen and a liquid containing 63 per cent. of nitrogen. A partial separation of the mixture will thus be effected, but to produce pure oxygen and pure nitrogen this process must be frequently repeated.

If air containing carbon dioxide be allowed to bubble through water, a considerable quantity of carbon dioxide will be dissolved. If the water be continuously replaced, a stationary state will be reached in which the air leaving the water will be practically free from carbon dioxide, though it will, of course, be saturated with water vapour. The composition of the liquid phase will differ very strongly from that of the gas with which it is in equilibrium, the former containing much more water and much less air than the latter. In this way air may be partially freed from carbon dioxide and, if required, the carbon dioxide may be regained by heating the water.

If air containing traces of acetylene be passed through a filter of active carbon, some air and acetylene will be adsorbed. However, since charcoal adsorbs acetylene much more eagerly than air, the ratio of acetylene to air in the adsorbed phase will be much greater than in the gas. If sufficient fresh charcoal is used, the air leaving the filter will be practically freed from acetylene. In this case, a continuous process requires the carbon to be circulated through the apparatus like a fluid —a problem which has only recently been solved.

If a mixture of argon and oxygen be passed over heated sulphur, the sulphur will be oxidized and the oxygen thus removed from the mixture until its partial pressure is equal to the dissociation pressure of sulphur dioxide, which is negligibly small. In this case a stable chemical compound is formed, which cannot easily be decomposed. Thus the oxygen

may be considered to have vanished permanently from the system and the process is no longer to be regarded as simple gas separation.

The processes employed in industry for separating the various gaseous mixtures reviewed in Chapter I of this book are based primarily on liquefaction at low temperatures. The other methods of bringing about two-phase equilibrium play a subsidiary role, in that they are used primarily to remove certain impurities, present in small quantities, either before the main separating process commences or after it has been completed. For this reason a knowledge of the vapour–liquid equilibrium of systems containing more than one component, which is treated theoretically and experimentally in Chapter II, is of paramount importance for the design and understanding of industrial separating plant. The plant itself, in which the actual separation is effected, in spite of all superficial diversities, is always essentially a combination of a few standard parts or units. These are described in Chapter III and their scope and purpose briefly summarized. Chapter IV contains the general theoretical equipment needed to describe what happens inside a fractionating plant and to calculate numerically the results to be expected under given conditions. Certain special theoretical problems that appear in particular cases are discussed later as they arise. In Chapter V refrigeration is treated in its relation to gas liquefaction and separation, and the various methods of gas liquefaction are analysed.

The first gas to be separated on a large scale by low-temperature methods was atmospheric air. It is therefore natural that most of the theory and a great deal of the practical experience of gas separation was gained by studying this particular mixture. In Chapters VI, VII, and IX the various problems are discussed which have arisen in connexion with the separation of air into oxygen, nitrogen, and the rare gases, and the several solutions of these problems are examined. The characteristics of fractionating columns are treated in Chapter VIII mainly in conjunction with air separation, but the results of this chapter are equally valid for the distillation of other mixtures.

With the production of commercial hydrogen from coke-oven gas, certain new questions arise, connected firstly with the complexity of the mixture and secondly with the very low boiling-point of hydrogen, which, at the temperatures subsisting in the plant, may be considered as a 'permanent gas'. These questions are discussed in Chapter X.

Chapters XI and XII deal principally with hydrocarbons and their production in a pure state from coke-oven gas and oil gases. The separation of helium from natural gas is also treated in this context.

I

GASES AND THEIR USES

THE raw materials from which most pure gases are obtained can best be divided into two groups, one of which consists of atmospheric air alone and the other contains all the further gaseous mixtures which will be treated in this book.

The composition of the earth's atmosphere, which is very accurately constant in respect to time and place, is given in Table 1. The concentrations are in *mole per cent.*

TABLE 1. *Composition of Atmospheric Air*

Nitrogen	78·03	Hydrogen	1×10^{-2}
Oxygen	20·99	Neon	$1{\cdot}5 \times 10^{-3}$
Argon	0·93	Helium	5×10^{-4}
Carbon Dioxide	0·03	Krypton	$1{\cdot}1 \times 10^{-4}$
		Xenon	$0{\cdot}8 \times 10^{-5}$

Only the hydrogen and carbon dioxide content varies slightly. It is apparent that, for most practical purposes, air may be considered as a binary mixture of nitrogen and oxygen, which together make up 99 per cent. of the whole. The influence of argon and the other rare gases on the production of pure oxygen and nitrogen and the methods evolved to extract these rare gases themselves and isolate them in a pure state will be discussed in Chapter IX.

All the other gaseous mixtures with which we shall have to deal may be classed as 'organic gases' from the fact that they are all the results of the transformation of organic matter. They are frequently divided into 'natural' and 'artificial' gases, the former term being applied to those emitted at many places on the earth's crust and the latter to those produced as a result of industrial processes.

The natural gases, such as marsh gas, earth gas, fire-damp, dry and wet oil-gases, and casing-head gas, differ notably in composition from the 'artificial' coal and coke-oven gases and from those evolved during the cracking of mineral oils. The natural gases contain only saturated hydrocarbons, together with varying amounts of nitrogen and carbon dioxide and occasionally small admixtures of helium. In the latter olefines occur as well as paraffins, together with large amounts of hydrogen. All coal gases contain nitrogen, carbon monoxide, and carbon dioxide in varying proportions.

The organic gases may reasonably be subdivided into those produced

from coal and those produced from, or more or less closely connected with, mineral oils. Of the former the best known are coal gas (or town's gas), coke-oven gas, low-temperature carbonization gas, producer gas, and water gas, and the gases obtained by the hydrogenation of coal and lignite. Of the latter we must mention natural gas, casing-head gas, and the similar gases obtained by 'topping' or 'stabilizing' petroleum, together with 'cracker gases' and those gained from oil hydrogenation. The fact that natural gases are often found in districts devoid of mineral oils shall not deter us from including them in this category.

Historically the first gas to be put to large-scale commercial use was coal gas, obtained by distilling coal in closed retorts in the absence of air, steam, or any other foreign agent. The town's gas industry developed so rapidly in the nineteenth century, especially in England, that it quickly assumed a dominant position, to such an extent that, in most people's minds, 'gas' is equivalent to the particular mixture supplied for cooking, heating, and lighting. At a time when the oil and coke industries are producing vast quantities of gaseous mixtures of widely differing compositions, it is still unusual to consider whether the mixture supplied to our homes is particularly suited to its purpose and whether it might not be better utilized otherwise, possibly not as fuel at all.

The composition of coal gas varies to a lesser degree according to the

TABLE 2. *Composition of Coal Gas produced at Various Temperatures*

Temperature (C.):	*750–900°*		*995°*	*1,370°*
Locality:	*London cannel coal*	*Heidelberg bituminous coal*	*Derbyshire gas coal*	
CH_4	41·99	42·40	32·9	32·6
C_nH_m	10·81	7·27	3·8	3·5
H_2	35·94	44·00	48·6	56·4
CO	10·07	5·73	5·6	7·5
CO_2	1·19	0·37	2·2	..
N_2	..	..	6·6	..

coal used and to a greater extent with the temperature of distillation. In former times, when coal was distilled at 700–800° C., the principal constituents were light hydrocarbons, methane, ethylene, and a certain amount of ethane, and it was these gases, together with small quantities of benzene vapour, that produced the characteristic luminosity of the gas flame. After the invention of the gas mantle, which made luminous flames unnecessary, and of better refractory materials, the temperature

in the retorts was gradually raised to 1,100–1,300° C., with the result that the percentage of hydrocarbons in the gas went down and that of hydrogen increased. In Table 2 some typical figures are given for the composition of coal gas produced at various temperatures.

The products of coal distillation are gas, coke, tar, and ammonia, but the gas industry is primarily interested in the gas. On the other hand, a very similar process, carried out in the coke-oven, produces primarily metallurgical coke and, as a by-product, coke-oven gas. The composition of this gas differs only slightly from that of coal gas, as the figures of Table 3 demonstrate, in which typical results of analysis of coke-oven gas are given from different sources.

TABLE 3. *Composition of Coke-oven Gas*

	Durham	*Lancs.*	*Yorks. and Derby*	*New York*	*Detroit*	*Saar*
CH_4 . .	28·0	33·9	30·0	25·5	23·5	26·5
C_nH_m . .	3·2	3·7	2·9	2·7	4·8	3·2
H_2 . .	48·0	49·1	50·0	48·7	43·2	51·4
CO . .	6·5	6·4	7·2	10·4	14·0	6·4
CO_2 . .	2·5	2·5	2·1	4·7	3·4	2·9
N_2 . .	11·8	4·4	7·2	8·0	11·1	9·4

The similarity of the two gases is not surprising when we consider that the process occurring in the retort is practically identical with that in the coke-oven. In both the coal is heated to about the same temperature in a fire-clay chamber, but whereas the retort is a small narrow vessel holding some 12 cwt. of coal, the charge of a coke-oven is from 15 to 25 tons. The retort is fired with producer gas, while the coke-oven is generally heated with a portion of the gas it yields. Usually 6 to 12 retorts are fired together in a single furnace or 'setting', while coke-ovens are arranged in batteries of 25 to 30 units. These are flat rectangular chambers, which may be 40–45 ft. long, 12–20 ft. high, and 14–20 in. wide. After periods of carbonization varying from 12 to 22 hours, the coke is forced out with a ram and quenched. From the point of view of gas-making, the chief advantage of retort distillation is that it is far more flexible than carbonization in coke-ovens.

Whereas the gas industry developed particularly rapidly in England, the coke industry, and with it the production of coke-oven gas, is more evenly distributed over the various countries. This is mainly due to the fact that it developed later, at a period when Britain had lost her monopoly position in industry. It is also connected with the fact that a greater variety of coals can be treated in coke-ovens than in retorts.

Low-temperature carbonization gas is a by-product of a process for producing a soft and easily ignitable semi-coke for domestic use. It is essentially similar to the gas formerly obtained in retorts at low temperatures, but contains rather more methane. Table 4 shows some typical examples.

TABLE 4. *Composition of Low-temperature Gas produced according to Various Methods*

	(1)	(2)	(3)
CH_4† . . .	39·6	48	67
C_nH_m‡ . .	4·3	13	6
H_2 . . .	37·2	27	12
CO . . .	6·1	7	5
CO_2 . . .	4·0	3	4
N_2 . . .	8·8	2	6

† Contains a little ethane.
‡ Ethylene and propylene.

At present this process is not carried out on a very large scale and the gas is therefore available in insufficient quantities to be of interest from our point of view.

As against the above-mentioned gases, *producer gas* and a number of similar mixtures are the products of processes for the complete gasification of coal and coke. Whereas a great part of the calorific value of coal is left in the coke after distillation, gasification transfers the whole of this calorific value to the gas, though not in a very concentrated form. The specific calorific value of the gas itself is not high, as it contains practically no hydrocarbons and is adulterated with varying amounts of nitrogen and carbon dioxide. This is due to the fact that the gases are produced by passing steam or air over hot coal and coke.

The best-known gases of this type are producer gas proper, Mond gas, and water gas. All these mixtures are produced in large quantities and are relatively cheap. Their approximate compositions are given in Table 5.

TABLE 5. *Composition of Gases of the Producer Gas Type*

	Producer gas	*Mond gas*	*Water gas*
CH_4 . .	3	4	0·5
C_nH_m . .	0·2	0·3	. .
H_2 . .	12	25	49
CO . .	28	12	42
CO_2 . .	3	16	5
N_2 . .	54	43	3

The hydrogenation of coal, or the synthetic oil industry, was specially developed in Germany with the object of making the country independent of oil imports. Similar work is being taken up in other countries, including Britain. The gases produced are similar to those obtained in the cracking and hydrogenation of mineral oil and motor spirit.

Turning from coal to oil, we have first to consider natural gas. Vast quantities of this gas are emitted at numerous places, especially in the U.S.A., Canada, and the U.S.S.R., and gradually larger and larger quantities are being used. It occurs as casing-head gas in most working oil-wells, where it is obviously to be considered as very light petrol. It also occurs, removed from actual oil wells but generally in oil-bearing districts, accompanied by greater or lesser quantities of oil that may be extracted from it. Gases containing more than 1 gallon of oil per 1,000 cu. ft. are often termed 'wet' gases. The rest are known as 'dry'. But apart from these, immense gas wells have been discovered in districts far removed from any vestiges of oil. It is suggested by some that this gas has migrated from oil-bearing districts through porous strata. Others believe that it has been formed quite independently of oil by some other natural process and from some other raw material.

The chief component of most natural gas is methane. The methane concentration varies from about 40 to well over 99 per cent. The other constituents are other light paraffins, mainly ethane and propane, and some nitrogen. Some natural gases also contain small quantities of helium, varying from the minutest trace up to as much as 2 per cent. Table 6 gives the compositions of some natural gases from various sources.

The total world utilization of natural gas in 1947 was about 4×10^{12} cu. ft., of which $3{\cdot}5 \times 10^{12}$ cu. ft. fell to the United States. This is only a small fraction of the gas emitted annually from the earth's surface.

Cracking is the name given to a number of processes employed mainly to increase the quantity of petrol obtainable from crude oil and to improve its quality for burning in cars and aircraft. It consists in subjecting the oil simultaneously to high pressures and high temperatures. The effect is to break up the large hydrocarbon molecules, and this leads to the formation of considerable quantities of free hydrogen. It also serves to rearrange the molecules in different configurations, and various results may be obtained according to the pressures and temperatures and according to whether a catalyst is used and, if so, depending on the nature of the catalyst. More recently cracking processes are

TABLE 6. *Composition of Natural Gases*

U.S.A.

	Monroe, La.	*Amarillo, Tex.*	*Columbus, Ohio*	*Ashland, Ky.*	*Hughston, Kans.*	*Ashley, Utah*
CH_4	94·7	72·94	80·4	75·0	68·86	99·42
C_2H_6	2·8	18·96	18·1	24·0	17·51	..
CO_2	0·2	0·39	0·0	0·0	0·10	0·20
N_2	2·3	7·71	1·5	1·0	13·33	0·24

(*Amer. Institute of Mining and Metallurgical Engineers*, **94**, 398 (1931); **107**, 347 (1934).)

U.S.S.R.

CH_4	99·8	99·6	97·8	89·8	82·1	77·5	57·6	40·5†
C_2H_6	..	..	..	..	2·1	2·0	16·8	..
C_3H_8	..	..	..	..	..	1·3	15·0	..
C_4H_{10}	..	..	..	..	..	..	10·2	..
Air or N_2	..	..	2·0	8·7	9·7	1·0	..	59·5†

† Private information.

(*The Science of Petroleum*, ii. 1507.)

POLAND

CH_4	78·8	72·2
C_2H_6	12·6	13·1
C_3H_8	6·1	1·5
C_4H_{10}	2·5	2·2
Air	..	11·0
H_2S	..	..

(Private information.)

IRAN

CH_4	81	36
C_2H_6	16	32
C_3H_8	..	9
C_4H_{10}	..	15
Air	2	1
H_2S	1	7

(Private information.)

Helium-bearing Natural Gases

U.S.A.

	Dexter, Kans.	*Eureka, Kans.*	*Petrolia, Tex.*	*Pearson, Okla.*	*Augusta, Kans.*
CH_4	14·85	51·80	56·85	59·33	74·74
C_2H_6, etc.	..	..	10·33	0·00	12·92
CO_2	..	..	0·25	0·00	0·19
O_2	..	..	0·54	0·45	0·57
N_2	82·70	46·40	31·13	39·59	11·08
He	1·84	1·50	0·90	0·63	0·50

(*Handbuch der anorganischen Chemie*, 1928, vol. iv, part 3, section 1, p. 44.)

CANADA

	Hamilton, Ontario	*Calgary, Alberta*	*Moncton, N.B.*
CH_4	80	87·6	80
C_2H_6, etc.	12	0·9	7·2
N_2	8	11·2	12·8
He	0·34	0·33	0·064

(*Handbuch der anorganischen Chemie*, 1928, vol. iv, part 3, section 1, p. 48.)

being used with the express purpose of producing materials for the chemical industry from crude oil and various oil fractions.

In all cracking processes large quantities of gas are developed, consisting mainly of light hydrocarbons and hydrogen. The composition varies greatly, but is usually maintained within the following limits:

TABLE 7. *Composition of Cracker Gas*

CH_4	25–45
C_2H_4	15–30
C_2H_6	6–12
C_3H_6	5–15
C_3H_8 and higher hydrocarbons	10–15
H_2	5–20

The total production of cracker gas in the U.S.A. in 1946 was approximately 3×10^{11} cu. ft. Very similar gases are evolved during the hydrogenation of oil and coal for the production of synthetic motor spirit.

Finally, one more type of organic gas should be mentioned, and that is *sewage gas*. In the course of the digesting process employed for the disposal of sewage, a gas is developed, consisting of 70 per cent. methane and 30 per cent. carbon dioxide. In up-to-date sewage works this gas is utilized as fuel. In the West Middlesex Main Drainage Works at Isleworth, 480 million cu. ft. of sewage gas are produced annually, which is mainly converted to power and utilized on the spot. Similar conditions exist in Birmingham and in several continental and American towns. The world production of sewage gas is increasing rapidly and the total output will soon be of the same order of magnitude as that of other better-known organic gases.

The foregoing review, though necessarily incomplete, will serve to convey some idea of the extent and nature of the manifold gases surrounding us. It will also show how uneven is the technical development in this sphere. Some gases, such as coal gas, have been known for over a century and have a long tradition of usefulness in the minds of the public. Natural methane-bearing gases have been known to exist from time immemorial, but only in recent years have they begun to play a part in economic life. Cracker gases and the similar products of hydrogenation are comparatively recent achievements and are the result of the development of the motor-car industry with its rising demand for particular types of petrol. The all-pervading atmosphere is perhaps the most flagrant example of delayed development. For many millions of years we have done nothing but breathe it, and not

till the last generation have we learned to weld with one of its components, produce fertilizers with a second, light our homes with the help of a third, and advertise our products with the glaring red light from a fourth.

In view of these facts it is not surprising that the utilization of gas, at the time of writing, is largely haphazard. Certain gases are used for certain purposes, not because these are the most rational ways of using them, but because they were or appeared to be rational fifty years ago, and since then so much capital has been invested in them that it was unprofitable to make any extensive changes.

The only gas that is now more or less rationally exploited is atmospheric air. Apart from numerous processes in which air is employed in an unchanged condition, such as the gasification of coal and the production of steel, air can be separated into oxygen and nitrogen and the various rare gases. For the last forty-five years oxygen from the air has been used to an increasing extent for cutting, welding, and similar purposes. Up to the First World War, oxygen was the only constituent of air to be utilized on a commercial scale. In the early twenties, with the advent of synthetic fertilizers, increasing quantities of nitrogen were in demand. Now large amounts of nitrogen are combined with hydrogen to form ammonia, which is the basis of the fertilizer industry and also incidentally of the production of most important explosives. At about the same time it was found profitable to fill incandescent lamps with argon, as this gas, with its high atomic weight, prevents vaporization of the filaments and thus allows the lamps to be maintained at a higher temperature than when filled with nitrogen, with a corresponding economy in the cost of candle-power.

In recent years attempts have been made to replace argon with mixtures of krypton and xenon, whose atomic weights are still higher. The extraction of krypton and xenon from air is a difficult task, owing to their very low concentrations; but the problem has been solved in principle and the commercial exploitation of these gases is now beginning.

Neon is now being used in considerable quantities in discharge tubes owing to the brilliant red light which it emits and which gives it great advertisement value. The blue light from argon is also useful in this connexion. Other possibilities of utilizing neon have been suggested, but have hitherto not been put into practice.

The extraction of helium from air is not a commercial proposition, since helium may be obtained more cheaply from natural gases.

From the point of view of some world-planning authority seeking to employ all gases to the greatest advantage of the community, it would appear rational to distinguish the following three groups of constituents in organic gases:

1. Hydrogen and carbon monoxide.
2. Paraffins.
3. Olefines and other unsaturated hydrocarbons.

1. Hydrogen and carbon monoxide have comparatively low calorific values but valuable chemical properties. Their utilization as fuel would appear uneconomical in a very general sense. The most rational utilization of hydrogen should be for synthetic ammonia and hydrogenation, and carbon monoxide should, for the same reason, be used preferably for various chemical syntheses.
2. The light paraffins that form constituents of gaseous mixtures are methane, ethane, propane, and butane. All have high calorific values and are chemically more or less inert. They should be used preferably as fuel and varied according to local conditions.
3. Though ethylene, propylene, and butylene form excellent fuel, they are too valuable to be used as such, as they have very useful chemical properties. They should be utilized preferably in chemical industry.

Clearly these complex problems cannot be solved superficially in the way indicated. The suggestions set forth above are not to be considered as a solution but are rather intended to point out that the problems exist at all. They have purposely presupposed that all the constituents named can be extracted from the crude mixtures available and that any difficulties in the process of separation are to be neglected in discussing rational utilization. It is one of the objects of this book to show that this standpoint is justified. The problem of separating gases into more or less pure components is in fact solved, in the sense that the fact of a certain constituent appearing in a mixture with other constituents is no longer an argument in favour of its being utilized together with these other constituents. This is a new and important fact which, it must be realized, is ushering in a new period of industrial development.

Let us now consider how organic gases are in fact being utilized, beginning with *Natural Gas*. In the U.S.A., Canada, and the U.S.S.R. large quantities of natural gas are used for domestic and industrial heating, although in all cases the amounts so used are only a small portion of what is emitted and much greater quantities are still wasted.

A number of towns are connected to the gas wells by pipe-lines, some of which are many hundreds of miles long. Both in Canada and the U.S.A. the consumption of natural gas is greater than that of coal gas. Since these gases consist mainly of methane, this method of utilization would appear rational. Considerable quantities of methane are also used for the manufacture of carbon black, which, with the present technique, is rather a wasteful process.

In spite of its limited reactivity, methane from natural gas is being used on an increasing scale for chemical purposes. In Germany it has been used for the production of acetylene by the electric-arc process and by partial oxidation, and in the U.S.A. a large plant is now under construction in which 50 million cu. ft. per hour of methane are to be treated with oxygen to form CO and H_2 for synthesis to oils and various oxygenated compounds.

The correct utilization of natural gas is a serious problem. The gas is available in very large quantities, but generally far removed from the consuming centres. It is difficult to store and transport and, in view of its inert nature, its chemical utilization is economical only because it is cheap. Its proposed use as a raw material for synthetic oil is due to the threatening oil scarcity in the United States, and it has been estimated that the potential reserves of oil from this source are of the same order as those of natural oil. Legal measures have been introduced in the United States to preserve the large supplies of gas available in the oil wells themselves, as the tapping of this gas reduces the pressure of the oil, thus lowering the yields from the wells and necessitating expensive pumping.

No use has yet been made of the excellent anti-knock properties of methane in internal combustion engines. It could provide a very high-grade fuel for aero-engines and for cars and lorries, but the difficulties connected with its low boiling-point have hitherto prevented its use for this purpose on a commercial scale. Its storage on vehicles in high-pressure gas containers is unpopular in view of the weight of the cylinders, and its use as a cold liquid necessitates vacuum-jacketed containers and other auxiliary equipment. Successful large-scale experiments have been carried out in England† on the use of liquid methane on lorries and buses, and the necessary equipment has been designed. However, England has no large reserves of natural gas, and the methane would have to be taken from other sources in which its concentration is lower.

† A. C. Egerton, T. A. Hall, and M. Pearce, *Journ. Inst. of Fuel*, **19**, 193 (1946).

One of the advantages of natural gas as a domestic and industrial fuel, as compared with coal gas, is that it is relatively easy to liquefy. The great problem of gas supply is that of storage to cover peak load periods, and large gas holders are both expensive and unsightly. With the use of natural methane it is possible to replace these gas holders with liquid storage tanks. A tank $20 \times 15 \times 10$ ft. could hold as much methane as a two million cu. ft. gas holder, and would be very much cheaper. The costs of liquefaction are not prohibitive. The large-scale storage of liquid methane in tanks was undertaken in America at the beginning of the war, but unfortunately a serious explosion took place in a tank at Cleveland in 1940, which ruined the installation and cost a number of lives. Although a careful examination appeared to show that the accident was due to secondary causes which could easily be eliminated in future, it has quite understandably held up development in this field. More recently the problem has been taken up again in the U.S.S.R. and the new Saratov–Moscow gas pipe-line is furnished with underground liquid storage tanks to cover peak load requirements. It is understood that the Carpathians–Kiev gas line is to be similarly equipped.

The extraction of helium from natural gas is carried out on an industrial scale in the U.S.A. and the U.S.S.R. The American sources are by far the richest in the world, and it is there considered uneconomical to work with a gas containing less than 0·5 per cent. helium. Before the war the Russians were working with much lower concentrations. With the disappearance of the airship, the principal use of helium has ceased, but the gas is required for a number of other purposes, though in smaller quantities. It is used to dilute the oxygen in high-pressure diving bells as it does not dissolve in the blood like nitrogen, and thus avoids caisson disease. It is also used as an inert gas for the preservation of certain foodstuffs, and it is of great scientific interest in providing means of attaining very low temperatures. The normal boiling-point of helium is 4·2° K and, with its help, temperatures below 1° K can be attained by allowing it to boil under reduced pressure. It thus provides indirect means for attaining the very much lower temperatures now used in low-temperature physics, and the anomalous properties of one modification of liquid helium have given rise to many interesting experiments and have thrown new light on the structure of matter.

A much more complicated state of affairs is apparent when we consider the utilization of the better-known organic gases, coal gas and coke-oven gas. As we have seen, the compositions of these two gases

are almost identical and the quantities of each produced in the world are of the same order of magnitude of 10^{12} cu. ft. per annum. But whereas coal gas is used almost exclusively for domestic lighting and heating, coke-oven gas has found a variety of applications. Part of this gas is used for the same purpose as coal gas, especially in Germany and in other countries with a large coke industry. Part is used in the coke ovens and the metallurgical plants, when these are attached to them. A good deal is wasted, and in some countries, particularly Germany and the U.S.S.R., large quantities of coke-oven gas are separated to yield hydrogen for the synthetic ammonia and hydrogenation industries. The remaining constituents, loosely termed rich gas, are mostly used as fuel. The separation of coke-oven gas is one of the most highly developed processes of low-temperature industry and will concern us at some length in Chapters X and XI.

With the increasing importance of olefines as raw materials for the chemical industries, and the lack of other more prolific sources in Britain and many other countries, attempts have been made to extract ethylene from coke-oven gas, in spite of its low concentration of about 2 per cent. Experimental work was done in this field in Russia some ten years ago, and in Germany during the last war the plants built to provide hydrogen–nitrogen mixtures from the gas were adapted to separate the rich gas also. Quite recently an ingenious plant has been built in England by the British Oxygen Co. to produce mainly ethylene, with some methane, from coke-oven gas, without extracting the hydrogen. This plant will be discussed in Chapter XI.

The utilization of cracker gases and similar products from the oil-refining industry is a new problem, just as these gases are themselves new. Much is still burned in spite of the valuable olefines which it contains. In America and the U.S.S.R. a number of plants have been built to extract ethylene and propylene from cracker gases, and butylene and butadiene are also obtained in this way. The products are used to make alcohols, synthetic rubber, plastics, and a number of other valuable substances. Whereas in most American and Russian plants the cracker gas is a by-product and the main purpose of the process is to produce high-grade petrol, plants are now being erected in England in which the gas is one of the principal products, and one of the main objects of the process is to produce olefines for the chemical industry.

Synthetic gases in European countries and natural gases in Canada and the U.S.A. have yielded considerable quantities of propane and butane, which are useful for domestic heating and as motor fuel. Their

advantage consists in the fact that they can be liquefied at room-temperature at fairly low pressures and are thus easy to store and transport. Their use as domestic fuel is largely confined to districts remote from industrial centres that have not yet been supplied with gas mains. Here 'bottle gas' (or 'calor gas'), as it is called, is a very welcome substitute.

II

THE EQUILIBRIUM OF GASEOUS AND LIQUID MIXTURES

1. The equilibrium of binary mixtures

THE state of a homogeneous system, consisting of more than one component, is completely defined by temperature, pressure, and the mole fractions x_1, x_2,..., x_{n-1}, where n is the number of components in the system. The remaining mole fraction x_n is then given by the relation $\sum_1^n x_i = 1$. In the case of a binary system, p, T, and x may be taken as independent variables, where x is the mole fraction of one of the two components. Every set of values p, T, and x determines a state of the system, which thus has three degrees of freedom.

The presence of a second phase in equilibrium with the first reduces the number of degrees of freedom by one. Moreover, equilibrium can subsist only if the pressure and the temperature are the same in both phases. Therefore, of the four variables p, T, x_1, x_2, where the subscripts refer to the two phases, only two are independent. If p and T are fixed, only one set of values (x_1, x_2) corresponds to a state in which the two phases are in equilibrium. Within certain limits, to each pair of values p and T there exists a definite pair of values x_1 and x_2. x_1 and x_2 may both be considered as functions of p and T.

In a space with coordinates p, T, and x we may therefore picture two surfaces, which we shall call *equilibrium surfaces*, one depicting the states of the first phase and the other those of the second phase. Each point on one surface will be related to a certain point on the other surface by the fact that two phases in states denoted by these points are in equilibrium with each other. Two such corresponding points are known as *nodes*, and straight lines joining a pair of nodes are called *connodals* or *tie-lines*. All connodals are by their nature perpendicular to the (p, T) coordinate plane. Therefore no two connodals can ever intersect.

In general two corresponding nodes will not coincide. For though thermodynamics requires that the pressure and temperature be the same in both phases, no such demand applies to concentrations. Indeed, as was stated in the introduction, the whole point in the use of phase equilibrium for gas separation is that in the two phases the concentrations differ.

The space between the two equilibrium surfaces is known as the *inhomogeneous region*. A point in this region does not define a stable

state of the system. When brought into a state represented by a point in the inhomogeneous region, the system will separate into two phases, represented by the two ends of the connodal through that point.

Thermodynamic analysis points to the existence of four types of curves on the equilibrium surfaces, which have a particular physical significance. These curves give a good idea of what to expect in a binary mixture.

Curves of the first type are called *pure component curves*. They mark the intersection of the equilibrium surfaces with the planes $x = 0$ and $x = 1$. In these planes the mixture degenerates into a one-component system, in which x is either zero or unity in both phases. The pure component curves are simply the vapour-pressure curves of the two pure constituents.

Along certain curves on an equilibrium surface the tangential plane may be perpendicular to the (p, T) coordinate plane, so that $(\partial p/\partial x)_T = (\partial T/\partial x)_p = 0$. This may have one of two physical meanings. The two equilibrium surfaces may merge into each other along this curve and so become a single surface, like a loosely folded piece of paper;† or the two surfaces may touch along the curve, but nowhere else. In the first case the curve is known as a *critical curve*, in the second case it is termed a *curve of equal composition*.

These phenomena may be made clearer by considering sections parallel to the (p, x) or (T, x) planes. The equilibrium surfaces intersect these plane sections in curves, which are called *equilibrium curves*. In the neighbourhood of a point on the critical curve of the equilibrium surface, the (p, x) or (T, x) section has the form shown in Fig. 1. The critical point K is a point on the critical curve, which intersects the plane of the paper at this point. The two curves, representing sections of the equilibrium surface with the plane of the paper, merge into one at K. In this and in subsequent figures the shaded areas mark the inhomogeneous regions.

A (p, x) or (T, x) section near a curve of equal composition is shown in Fig. 2. L is a point on the curve of equal composition, which must again be considered as intersecting the plane of the paper at this point. In the case of Fig. 1 the critical nature of point K is immediately clear from the fact that we may pass freely around K from one phase to the other without traversing the inhomogeneous region. In the case of a point of equal composition, as shown in Fig. 2, this is not possible.

† The folded sheet of paper is an example of a surface which can be unfolded on to a plane. In general this will not be possible.

Finally, the system may pass into states in which a third phase makes its appearance. The effect of this is to remove another degree of freedom, so that these states must lie on one or more curves on the (p, T, x) surfaces. These *three-phase curves* may be considered as arising in the following manner. Each pair of phases in equilibrium gives rise

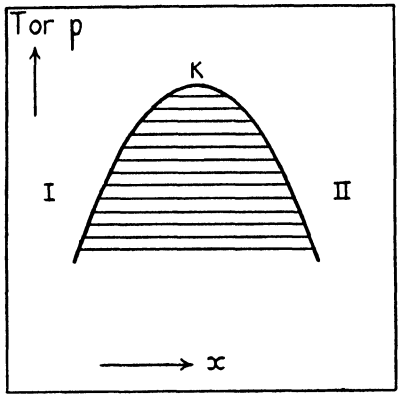


FIG 1. Equilibrium curve in the vicinity of a critical point. I and II denote the two phases

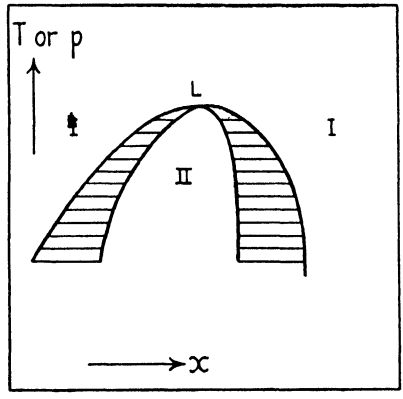


FIG. 2. Equilibrium curves in the vicinity of a point of equal composition

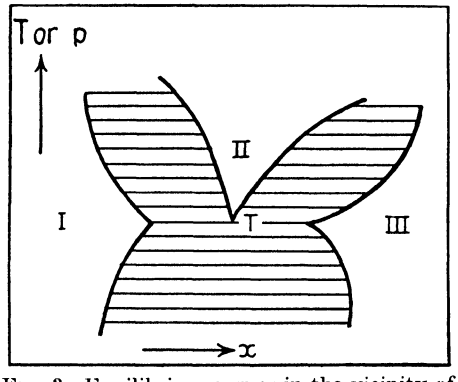


FIG. 3. Equilibrium curves in the vicinity of a triple point

to two surfaces. For three phases we thus have six surfaces: two refer to equilibrium between phase I and phase II, two between phase II and phase III, and two between phase III and phase I. If all three phases are to be in equilibrium together, the six surfaces must intersect in pairs in such a manner that the three curves of intersection shall have the same values of p and T at all their points. Fig. 3 shows a section of the three pairs of surfaces parallel to the (p, x) or (T, x) plane. Of the three points of intersection in Fig. 3 the inner point T

is known as the *triple point* and the locus of points T is called the three-phase curve.

We have discussed the typical forms of equilibrium diagrams in the neighbourhood of certain curves on the (p, T, x) surface. It is now

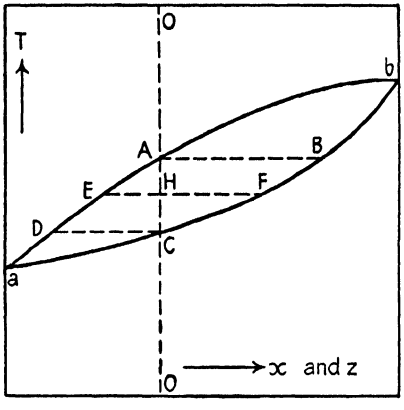


FIG. 4. (T, x) curves with pure component points a and b, showing process of condensation

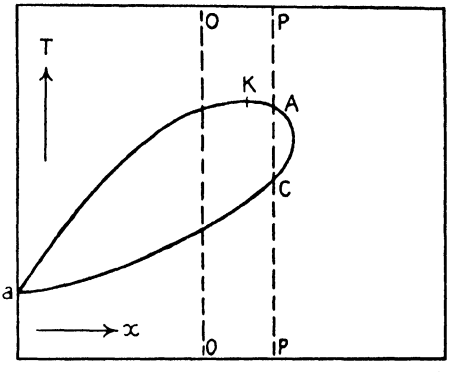


FIG. 5. (T, x) curves showing critical point K

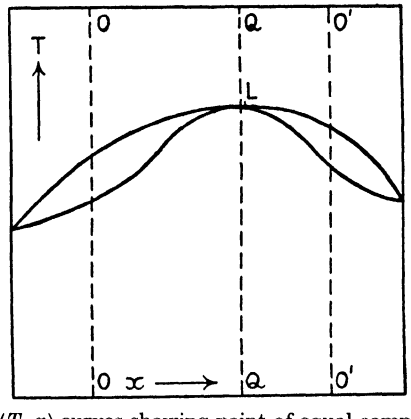


FIG. 6. (T, x) curves showing point of equal composition L

easy to combine these results to show the typical forms that equilibrium curves may assume across the whole (p, x) or (T, x) planes. These curves will be familiar to most readers from their knowledge of solid–liquid equilibrium. We shall first consider sections of the surface parallel to the (T, x) plane, or, as they are usually termed, (T, x) *diagrams*.

When the liquid phases are miscible in all concentrations, as is the case with all systems that will concern us here, three types of (T, x) diagram may appear, as shown in Figs. 4, 5, and 6. In Fig. 4, a and b

are pure component points, i.e. points on pure component curves on the corresponding (p, T, x) surface. Fig. 5 has a critical point at K and Fig. 6 a point of equal composition at L. K and L are points on the corresponding curves of the $(p,\ T,\ x)$ surfaces. Thermodynamics shows that K and L are always either maxima or minima on the (p, x) and (T, x) diagrams. As a rule the (p, x) diagram is similar in shape to the (T, x) diagram, but it is always inverted as regards the x-axis. For if a change in composition leads to a rise in vapour pressure at constant temperature, the same change in composition, carried out at constant pressure, will lower the temperature at which the two phases are in equilibrium. The curve bounding the inhomogeneous region and the vapour phase is frequently called the *dew-curve*; that bounding the inhomogeneous region and the liquid phase is known as the *boiling-curve*.

If a binary system, having equilibrium curves as shown in Fig. 4, is cooled at constant pressure along the dotted line O–O, condensation commences at the dew-curve at the point A and the first drop of liquid condensed has the composition of point B on the boiling-curve. In order that condensation may proceed, the temperature must be lowered further. The composition of the liquid shifts to the left along the boiling-curve and that of the vapour in the same direction along the dew-curve. Finally, when all the vapour has been liquefied, the liquid naturally has the same composition as the original gas (point C) and the last bubble of vapour is of the composition D.

At a point H between A and B, in the inhomogeneous region, the ratio of the amount of vapour and the amount of liquid present may be determined as follows. The total mass present is the sum of the mass of the liquid and that of the vapour, and the same relation applies to the mass of any one of the components. If M_x, M_y, and M_z be the mass of the liquid phase, the mass of the original mixture, and the mass of the vapour phase respectively, and if x, y, and z be the corresponding mole fractions of one of the two components,

$$M_y = M_x + M_z$$

and

$$M_y y = M_x x + M_z z;$$

whence

$$M_x/M_z = (z-y)/(y-x) = EH/HF.$$

This relationship is often called the *lever rule*. It is obviously applicable when M denotes any additive property and is not confined to the mass. The same rule will be applied frequently later when the specific enthalpy h is taken as the ordinate instead of the temperature T. We see in Fig. 4 that, as the temperature falls from A to C, the ratio $M_x/M_z = EH/HF$

increases from 0 to ∞. The amount of liquid gradually increases and the vapour vanishes.

The same phenomena occur if we cool the mixture along the dotted line O–O in Fig. 5 or along O–O and O'–O' in Fig. 6. However, things are different along the line P–P, situated to the right of the critical point K in Fig. 5. On cooling our mixture to point A the new phase formed is not a liquid but a gas. At any rate, it will appear at the top of the cooled vessel and not at the bottom, and we may conclude that the mixture we have been cooling was in fact not a gas but a liquid. On further cooling, this new vapour phase will at first increase in mass and then again decrease. At point C it will finally vanish altogether and only a liquid phase will remain. This phenomenon, which is called *retrograde condensation*, was discovered by Kuenen. It appears natural enough when we realize that, in a closed vessel, there is no way of distinguishing between a gas and a liquid as long as only one phase is present. It appears strange to us at first because we are used to liquids with free surfaces, i.e. bounded by air or vapour.

With the (T, x) curves of Fig. 5, and similarly with (p, x) curves, we cannot prove that the new phase formed is a vapour and not a liquid. The phenomenon becomes strikingly clear when we employ a (v, x) diagram, in which v is the specific volume. The (v, x) curves show at once that the new phase has a greater volume than the original mixture, i.e. a smaller density. However, we have refrained from introducing (v, x) diagrams as they are seldom used and might confuse the reader.

On cooling a mixture along the line Q–Q through the point of equal composition L on Fig. 6, complete condensation occurs at constant temperature as in the case of a pure substance. This is the principal characteristic of points of equal composition.

Fig. 5 may be considered as having developed from Fig. 4 with rising pressure. Consider a series of (T, x) curves at various pressures (Fig. 7). As the pressure is raised the curves gradually move upwards, since the boiling-point of a substance is raised when the pressure increases. Finally, the critical point of one of the components may be reached. The (T, x) curves above this pressure will break away from the ordinate axis corresponding to this component and, when the pressure is raised further, recede across the figure and finally vanish at the critical point of the other component.

Occasionally it may happen that the critical curve of the mixture begins below the critical point of either component. In this case the

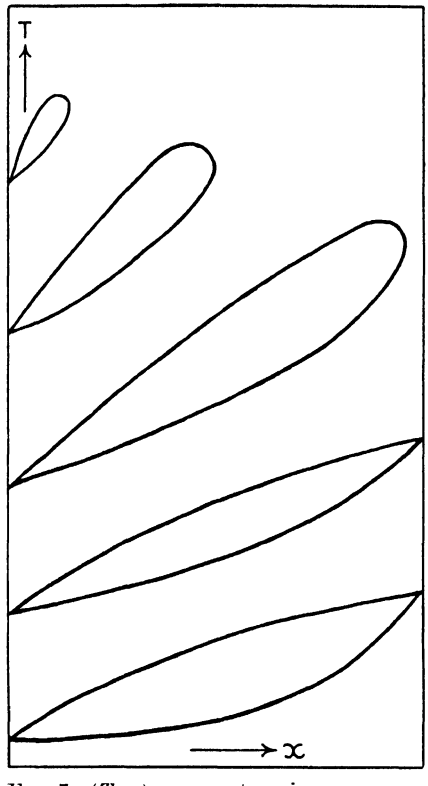


FIG. 7. (T, x) curves at various pressures above and below the critical point of one component

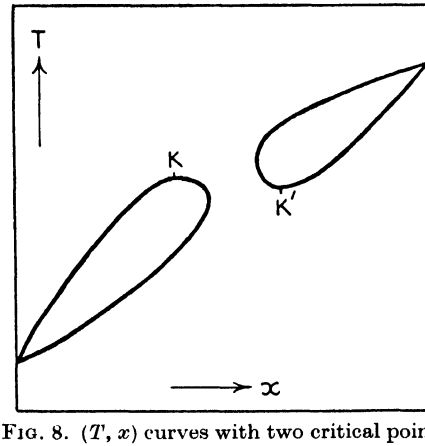


FIG. 8. (T, x) curves with two critical points

(T, x) curves break asunder in the middle of the diagram, as shown in Fig. 8. The phenomena of retrograde condensation occurring in this case may be inferred from the figure.

The following arguments, though they might be illustrated quite well on the (T, x) diagram, will appear more familiar in (p, x) coordinates. Consider a (p, x) diagram with a critical point, as shown at the top of Fig. 9. Suppose the critical point to be a maximum on the (p, x) curve.

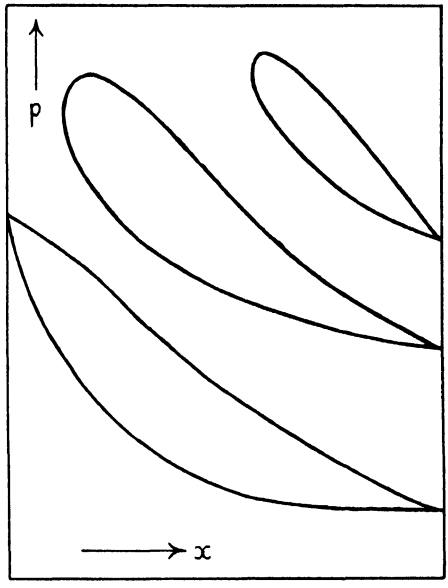


FIG. 9. (p, x) curves at various temperatures when critical points of components are close together

As the temperature is reduced the inhomogeneous region will move downwards, and we should expect it to spread across the diagram and finally lead to a pure component point, as in the (T, x) diagram of Fig. 7. In many cases this actually occurs, but occasionally the phenomena are different. The inhomogeneous region may spread out in all directions, as shown in Fig. 10, and finally the critical point may recede to indefinitely high pressures. In fact it will eventually reach the solidification curve. This type of equilibrium curve will frequently occur in subsequent sections and is characteristic of a mixture in which the critical points of the two components are far apart.

We have here discussed merely three types of curves on the (p, T, x) surface. The fourth type, i.e. the three-phase curves, will not concern us in future, so it will suffice to give the essential features in the (T, x) form in Figs. 11 and 12.

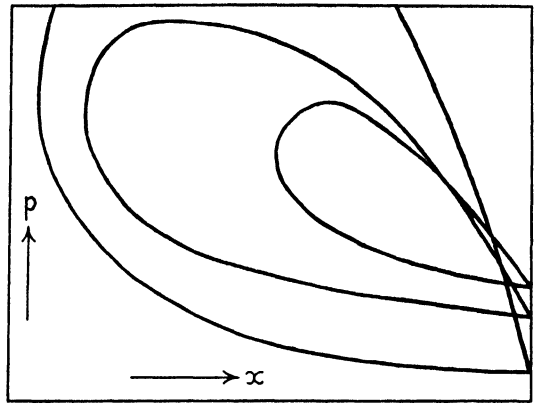


FIG. 10. (p, x) curves at various temperatures when critical points of components are far apart

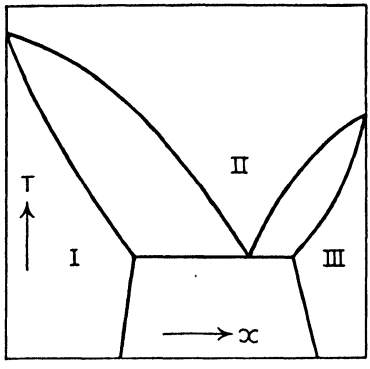


FIG. 11. (T, x) curves with triple point. Phase II exists above three-phase curve only

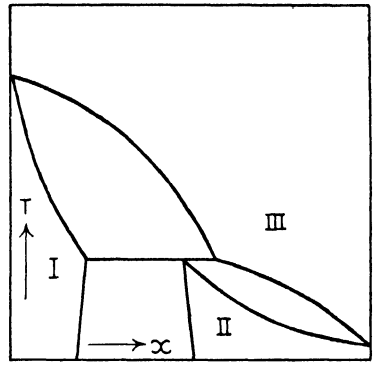


FIG. 12. (T, x) curves with triple point. Phase II exists below three-phase curve only

2. Ternary mixtures

A system of three components in two-phase equilibrium, as is clear from the beginning of the last section, has three degrees of freedom. The variables of the system, apart from temperature and pressure, are the two concentrations x_1 and x_2 of the components 1 and 2 in the liquid phase and the corresponding concentrations z_1 and z_2 in the vapour. The concentrations x_3 and z_3 of the third component are given by the relations $\sum_i x_i = 1$ and $\sum_i z_i = 1$. Thus, in addition to temperature and pressure, one concentration may within certain limits be chosen arbitrarily, after which all the other concentrations are fixed by laws of nature.

Since the concentration of one of the components of a homogeneous

ternary mixture can always be derived from the other two, it would be quite possible to represent the composition of a ternary mixture on a diagram in rectangular coordinates, one concentration being plotted as ordinates and the other as abscissae. All the compositions of the mixture would then be depicted by the points of an isosceles right-angled triangle, the two equal sides having unit length. For reasons of symmetry it is, however, more usual to use an equilateral triangle. The coordinate axes are then inclined to each other at an angle of 60° and the concentration of the third component can, if desired, be read off directly from the diagram.

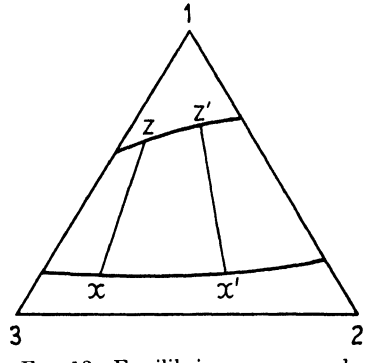


FIG. 13. Equilibrium curves and connodals of ternary mixture

Suppose now that, at a certain temperature and a certain pressure, we fix on a definite concentration z_1 of the first component in the vapour phase. If the concentrations are plotted on the triangular diagram as indicated in Fig. 13 for constant T and p, the choice of z_1 fixes two points $z = (z_1, z_2, z_3)$ and $x = (x_1, x_2, x_3)$ on this diagram. If we take another value of z_1, say z_1', then z_2 and z_3 will also change, as well as x_1, x_2, and x_3, and two new points will appear. The loci of all the points x and z will in general describe two curves on the triangle, a boiling-curve and a dew-curve. The area between these two curves is the inhomogeneous region. The straight lines joining two points x and z that are in equilibrium with each other are called connodals as in the case of binary mixtures.

As a rule, at a given temperature, two-phase equilibrium will not subsist at all if the pressure is lower or higher than the vapour pressures π_1, π_2, π_3 of all the components at that temperature. If

$$\pi_1 < \pi_2 < p < \pi_3,$$

there will be two-phase equilibrium between 1 and 3 and between 2 and 3, but not between 1 and 2. In this case the curves will cross the triangle in the way indicated in Fig. 14. If $\pi_1 < p < \pi_2 < \pi_3$, the curves will run as in Fig. 13.

If at the temperature in question a critical point occurs on the (p, x) diagram of one of the two-component systems of which the ternary system is composed, say 1 and 3, and if the pressure is higher than the critical pressure of this binary system at the temperature concerned,

the dew- and boiling-curves will not traverse the entire diagram but will merge into a single curve, as shown in Fig. 15. When a connodal degenerates to a point, that point is called a critical point of the ternary system. Here liquid and vapour become identical.

Suppose a quantity m_y of a mixture of the composition y_1, y_2, y_3 to be brought to a temperature and pressure corresponding to a point y in the inhomogeneous region of a triangular diagram. The mixture will

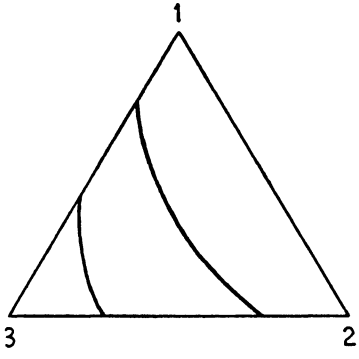


FIG. 14. Equilibrium curves of ternary mixture

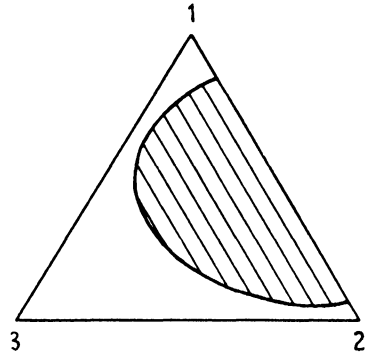


FIG. 15. Equilibrium curves and connodals of ternary mixture showing critical point

separate into a vapour phase z and a liquid phase x, and the following four relations will hold:

$$m_y = m_x + m_z,$$
$$m_y y_i = m_x x_i + m_z z_i \quad (i = 1, 2, 3).$$

Hence we can deduce that

$$(z_1 - x_1)/(y_1 - x_1) = (z_2 - x_2)/(y_2 - x_2) = (z_3 - x_3)/(y_3 - x_3).$$

This equation shows that y lies on a straight line through x and z just as in the case of binary systems.

Now let x and z be the points marking the phases into which a mixture y has separated. Then, just as in the case described on p. 18,

$$m_x/m_z = (z_1 - y_1)/(y_1 - x_1) = yz/yx.$$

In order to describe two-phase equilibrium of a ternary system in the way indicated, we need a separate triangle for every temperature and pressure. It is not practicable to plot a whole series of isobars and isothermals on one triangle, as the connodals would intersect and the diagram would be unintelligible.

Hausen† uses a rather more concise triangular diagram. The vari-

† H. Hausen, *Forschung auf dem Gebiete des Ingenieurwesens*, **6**, 9 (1935).

ables are here taken as p, z_1, and z_2. At a given pressure, any two values of z_1 and z_2 determine a point z on the triangle. To given values of z_1 and z_2 not more than one pair of concentrations x_1 and x_2 will correspond. Within certain limits every point z will correspond to a point x with which it is in equilibrium at some temperature or other.

In order to plot all the z's and x's on one readable diagram Hausen introduces, apart from the ordinary triangular coordinates, which are

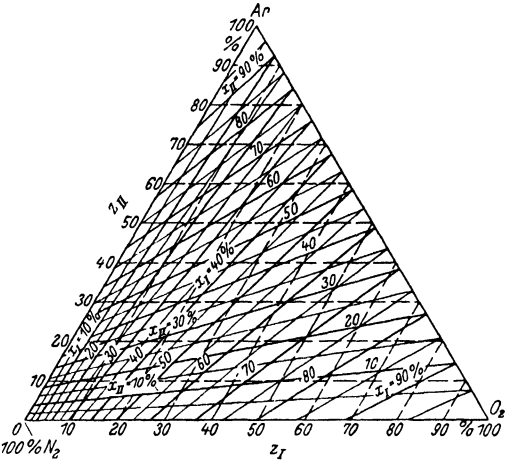


FIG. 16. Equilibrium curves of oxygen–argon–nitrogen mixtures at 1 atm. according to Hausen

x_I per cent. oxygen in liquid
z_I per cent. oxygen in vapour
x_{II} per cent. argon in liquid
z_{II} per cent. argon in vapour

used to describe the z's, a new set of coordinates on the triangle for the x's in such a way that two corresponding points x and z coincide. The new coordinates, which will in general be curved lines, are lines of constant concentration for one of the components in the liquid phase. The two sets of coordinates together describe all the equilibrium states of a ternary system at a given pressure and at all temperatures. However, temperature cannot be read off from this diagram, an example of which is shown in Fig. 16.

A further method of representing ternary mixtures has been used by Fischer.† Here a regular orthogonal (T, x) diagram is used, and equilibrium is shown at constant values of pressure and one concentration. This is achieved with three equilibrium curves in the following way. Let the compositions of the liquid phase be x_1, x_2, x_3 and those of the

† V. Fischer, *Annalen der Physik*, **21**, 426 (1934).

vapour be z_1, z_2, z_3, and suppose we have fixed x_1 = const. as well as p = const. Then the values of z_1 will be given as a function of temperature by the abscissae of one curve, and the values of z_2 will be given by the horizontal distance from this curve to a second curve. z_3 is then simply $1-(z_1+z_2)$. In the same way the values of x_2 are

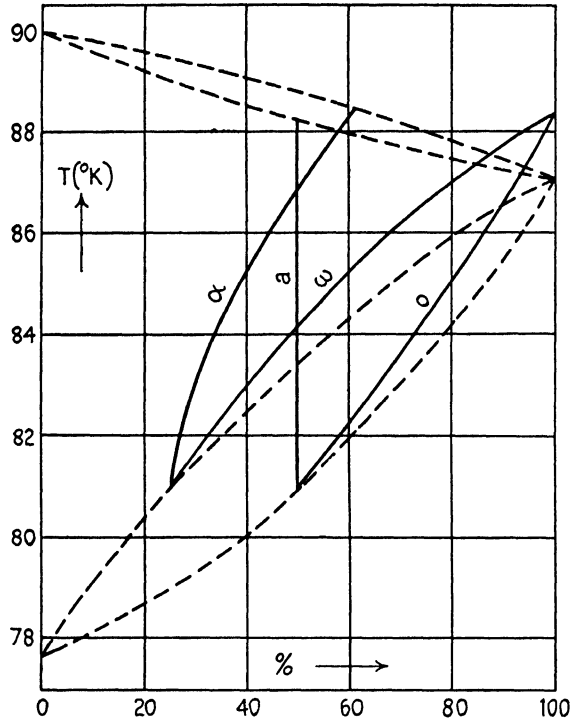


FIG. 17. Equilibrium curves of oxygen–argon–nitrogen mixtures at 1 atm. according to Fischer. Fifty per cent. argon in liquid

o oxygen in liquid $\quad$ a argon in liquid
ω oxygen in vapour $\quad$ α argon in vapour

given by the horizontal distances from the ordinate x_1 = const. to a third curve, and x_3 is $1-(x_1+x_2)$. The curves for the ternary system are bounded by the equilibrium curves of the corresponding binary mixtures.

In Fig. 17 the equilibrium of oxygen–argon–nitrogen mixtures at 1 atm. is represented in this way, as calculated by Fischer, the argon concentration in the liquid being fixed at 50 per cent. The dotted curves represent the oxygen–argon and nitrogen–argon equilibrium.

The principal advantage of this method is that it allows compositions to be read off as a function of temperature. It also enables a whole

series of curves for various values of the one fixed concentration to be plotted on one figure. However, it must be admitted that in this case the diagrams soon become rather confusing, since the curves of one group intersect those of other groups. But the method can be extended to systems of four and more components, which makes it valuable for some calculations.

3. Thermodynamic relations†

Hitherto our theoretical considerations have enabled us to determine only the number of independent variables of systems in two-phase equilibrium and the possible general shapes of the curves and surfaces that may, in a (p, T, x) space and its (p, x) and (T, x) sections, represent the boundaries between liquid and gaseous phases. It is in the nature of thermodynamics that it can give us no quantitative information as to the exact form of these curves and surfaces. This information, which is contained in equations of state, can be deduced only from molecular theory. The existing equations of state for liquid and gaseous mixtures are either too inaccurate to give the required results except in particular cases, or they contain so many specific constants that their use presupposes the existence of extensive experimental data concerning the mixtures in question. As a result of this, it has been necessary to determine the (p, T, x) relations of liquid mixtures in equilibrium with their vapours on the basis of direct experiment.

Nevertheless, especially at low pressures, when the state of the vapour is not too far removed from that of a perfect gas, some theoretical conclusions can be drawn.

(a) Changes in mixtures—the Gibbs–Duhem relation

It was stated in § 1 that a liquid and a vapour cannot be in equilibrium with one another unless the temperature and the pressure are the same in both phases. The laws of thermodynamics require yet a third condition to be fulfilled in the case of mixtures containing more than one component, and this is that the chemical potential μ_i of each component i shall be the same in both phases. One of several alternative definitions of the chemical potential is by the relation

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p}, \tag{1}$$

where n_i is the number of moles of the component i in the particular

† For the thermodynamics of mixtures and solutions see E. A. Guggenheim, *Modern Thermodynamics by the Methods of Willard Gibbs* (Methuen, 1933).

phase and G is the Gibbs potential, which is related to the energy E and the entropy S by the equation

$$G = E - TS + pV. \tag{2}$$

As we shall in future never use E in our calculations, but shall frequently require the enthalpy H, which is defined as

$$H = E + pV, \tag{3}$$

we can best write equation (2) in the form

$$G = H - TS. \tag{4}$$

G is here considered as a function of p, T, and the n_i, so that

$$dG = \frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial p} dp + \sum_i \frac{\partial G}{\partial n_i} dn_i, \tag{5}$$

for which we may write, using (1) and well-known thermodynamic relations,

$$dG = -S\, dT + V\, dp + \sum_i \mu_i\, dn_i. \tag{6}$$

Now consider a change at constant temperature and pressure in which the number of moles of each component is increased by the same fraction $d\lambda$ of the number already present, so that

$$dn_i = n_i\, d\lambda.$$

The composition of the mixture thus remains unaltered and, as temperature and pressure do not change, all those properties of the system, such as volume, enthalpy, entropy, etc., whose values for the whole system are equal to the sum of their values for its parts, will also increase by a factor equal to $d\lambda$ times their original values. Since the Gibbs potential is such a property,

$$dG = G\, d\lambda.$$

But for a change at constant temperature and pressure equation (6) gives $dG = \sum_i \mu_i\, dn_i$, and this is equal to $\sum_i \mu_i n_i\, d\lambda$, so that

$$dG = \sum_i \mu_i n_i\, d\lambda.$$

Equating coefficients, we thus obtain

$$G = \sum_i \mu_i n_i, \tag{7}$$

a relation which is evidently independent of the fact that the change we considered took place at constant temperature and pressure. Therefore

$$dG = \sum_i \mu_i\, dn_i + \sum_i n_i\, d\mu_i. \tag{8}$$

By comparing (8) with (6) we obtain

$$-S\, dT + V\, dp - \sum_i n_i\, d\mu_i = 0. \tag{9}$$

This gives a relation, valid in any phase, between changes of pressure, temperature, and composition. For the special case of isothermal changes at constant pressure

$$\sum_i n_i \, d\mu_i = 0. \tag{10}$$

This is known as the Gibbs–Duhem relation.

(*b*) *Two-phase equilibrium*

For the case of equilibrium between a liquid phase L and a vapour phase G, we have two equations of the form of (9). By subtracting one from the other we obtain

$$-(S_G - S_L)\, dT + (V_G - V_L)\, dp - \sum_i (n_{Gi} - n_{Li})\, d\mu_i = 0, \tag{11}$$

since $$\mu_{Li} = \mu_{Gi} = \mu_i.$$

For an isothermal change in a binary system we thus have

$$(V_G - V_L)\, dp - (n_{G1} - n_{L1})\, d\mu_1 - (n_{G2} - n_{L2})\, d\mu_2 = 0. \tag{12}$$

Replacing the n_i by mole fractions $x = n_{L1}/(n_1 + n_2)$ and $z = n_{G1}/(n_1 + n_2)$ and the volumes V by molal volumes $v = V/(n_1 + n_2)$, this equation becomes

$$(v_G - v_L)\, dp - (z - x)(d\mu_1 - d\mu_2) = 0. \tag{13}$$

In order to make use of these equations, we must know μ_1 and μ_2 as functions of pressure and composition. It is here that we must add to our thermodynamic relations knowledge obtained from an equation of state. From here on the equations are therefore no longer of general validity.

(*c*) *Vapour a perfect gas—Duhem–Margules equation*

The chemical potential μ_i of a component in a perfect gas mixture may be written in the form

$$\mu_i = \mu_i^0(T) + RT \log p_i, \tag{14}$$

where $\mu_i^0(T)$ depends on the temperature alone and p_i is the partial pressure of the ith component defined by

$$p_i = x_i p. \tag{15}$$

Then at constant temperature

$$d\mu_i = RT \, d \log p_i, \tag{16}$$

and if we replace moles by mole fractions, equation (10) reads

$$\sum_i x_i \, d \log p_i = 0, \tag{17}$$

valid for constant temperature and total pressure. This is known as

the Duhem–Margules equation. Since the μ_i of a liquid in equilibrium with a vapour are the same as those of the vapour itself, equation (16) will also hold for a liquid in equilibrium with a perfect gaseous mixture. The p_i are then partial vapour pressures.

Equation (13) for a binary mixture may then be written

$$(v_G - v_L)\,dp = (z-x)RT(d\log p_1 - d\log p_2). \tag{18}$$

If we write $p_1 = zp$, $p_2 = (1-z)p$, (18) becomes

$$(v_G - v_L)\,dp = RT\frac{z-x}{z(1-z)}\,dz. \tag{19}$$

When, as here, the vapour is a perfect gas, we may frequently assume that the pressure is so low that the specific volume of the liquid may be neglected as compared with that of the gas. Then the left side of (19) becomes $v_G\,dp = RT\,d\log p$, and we obtain

$$d\log p = \frac{z-x}{z(1-z)}\,dz, \tag{20}$$

valid for changes at constant temperature. This equation can be integrated according to a method proposed by Runge. It can then be used to calculate the dew-curve $z(p)$ of a binary mixture when the boiling-curve $x(p)$ is known. It should be remembered that (20) holds only at low pressures when the vapour may be considered to be a perfect gas and the molal volume of the liquid may be neglected.

(d) Imperfect vapour phase—fugacity of a component in a mixture

If the vapour is not a perfect gas, the chemical potential μ_i of component i in the mixture may be written

$$\mu_i = \mu_i^0(T) + RT\log f_i, \tag{21}$$

where f_i is the fugacity of i in the mixture, as defined by this equation and by the relation $f_i \to p_i$ when $p \to 0$.

This definition of the fugacity of a component in a mixture is a logical extension of its definition for a single gas:

$$\mu = \mu^0(T) + RT\log f \tag{22}$$

and

$$f \to p \quad \text{when} \quad p \to 0.$$

For a pure substance f can be determined in a number of ways from equations of state or directly from measurements of p–v–T relations. A method frequently used is that proposed by Lewis by means of the equation

$$RT\log f = RT\log p - \int_0^p \left(\frac{RT}{p} - v\right) dp. \tag{23}$$

The 'residual' in the brackets is the difference between the actual volume of the gas or liquid and the volume which it would have if it were a perfect gas.

The fugacity f_i of a component in a mixture, which appears in equation (21), can be determined for moderate pressures from the empirical relation

$$f_i = z_i f, \tag{24}$$

where f is the fugacity of pure i at the same total pressure and temperature and z_i is the concentration of i in the gaseous mixture. In this way

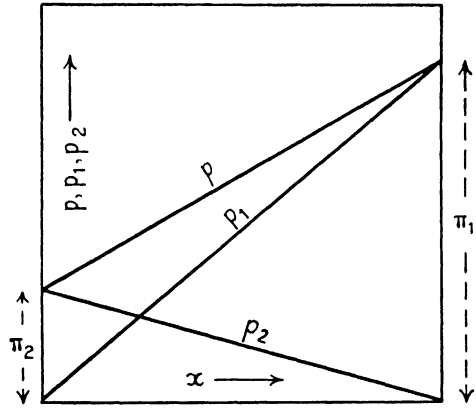


FIG. 18. Partial and total pressures of perfect binary solution

calculations based on equations (17) and (18) can be applied to systems with imperfect vapour phases by substituting f_i for p_i.

(*e*) *Perfect solutions*

The chemical potentials of a number of liquid mixtures conform to the equation

$$\mu_{iL} = \mu_{iL}^0 + RT \log x_i, \tag{25}$$

where μ_{iL}^0 depends on temperature and pressure but not on composition. These mixtures are known as *perfect solutions.*

Now for a vapour in equilibrium with a liquid $\mu_{iL} = \mu_{iG}$. If the vapour is a perfect gas, $\mu_{iG} = RT \log p_i$, and hence

$$\log p_i = \log x_i + \log k_i,$$

where k_i is independent of composition. When $x_i \to 1$, $p_i \to \pi_i$, where π_i is the vapour pressure of the pure ith component. Therefore $k_i = \pi_i$ and

$$p_i = \pi_i x_i. \tag{26}$$

That is to say, the partial pressure of the ith component in the vapour is equal to the vapour pressure of the pure component multiplied by the concentration of that component in the liquid phase (Fig. 18).

Equation (26) is known as *Raoult's Law*, which is valid for all solutic at sufficiently low concentrations. Perfect solutions are thus solutic for which Raoult's law holds for all concentrations.

By expressing p_i in the form $p_i = z_i p$, where z_i is the concentrati of i in the vapour, Raoult's law can be written

$$z_i = \frac{\pi_i}{p} x_i. \qquad (2$$

This equation enables z_i to be determined from x_i and vice ve provided the vapour pressures of pure i are known. For binary mixtu it relates the dew-curve and the boiling-curve in integrated form and much simpler than the differential equation (20). But, whereas (2 always holds if the vapour is a perfect gas, (27) is valid only if, addition to this, the liquid phase is a perfect solution.

If the vapour phase is not a perfect gas,

$$\mu_{iG} = RT \log f_i \quad \text{and} \quad \log f_i = \log x_i + \log k_i.$$

Moreover, when $x_i \to 1$, $f_i \to f_i^0$, where f_i^0 is the fugacity of pure i at t same temperature and at the vapour pressure corresponding to th temperature.

Hence for a perfect solution, the vapour of which is not a perfect g

$$f_i = f_i^0 x_i \qquad (2$$

where x_i is again the concentration of the ith component in the liqu phase, f_i the fugacity of i in the gaseous mixture, and f_i^0 its fugacity that temperature and at the vapour pressure corresponding to it.

Equation (28) is unsatisfactory in that we have no adequate mea of determining f_i, except for the empirical relation (24) mention above, which is valid only at moderate pressures. (28) and (24) togetl yield the equation

$$z_i = \frac{f_i^0}{f} x_i. \qquad (2$$

Here f_i^0 and f are both the fugacity of pure i at the temperature of t solution, but f_i^0 is taken at the vapour pressure of pure i at this tempe ture and f at the total pressure of the mixture under consideration.

Equation (29) is the natural analogy of Raoult's law (27) for a perf solution with a vapour which is not a perfect gas, but it must be point out that it is essentially an empirical relation, and should not be ext polated without due caution.

Krichevsky and Torocheshnikov† showed that mixtures of oxyg and nitrogen and of carbon monoxide and nitrogen could be descril

† J. Krichevsky and N. Torocheshnikov, *Zeitschr. f. phys. Chemie* (A), **176**, 338 (19

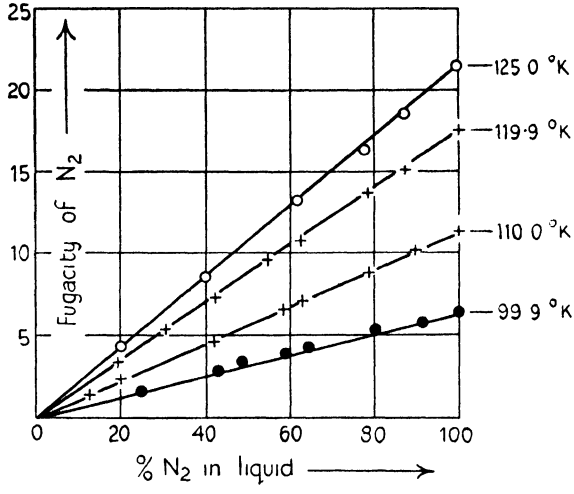


FIG. 19. Fugacity of nitrogen in nitrogen–oxygen mixtures

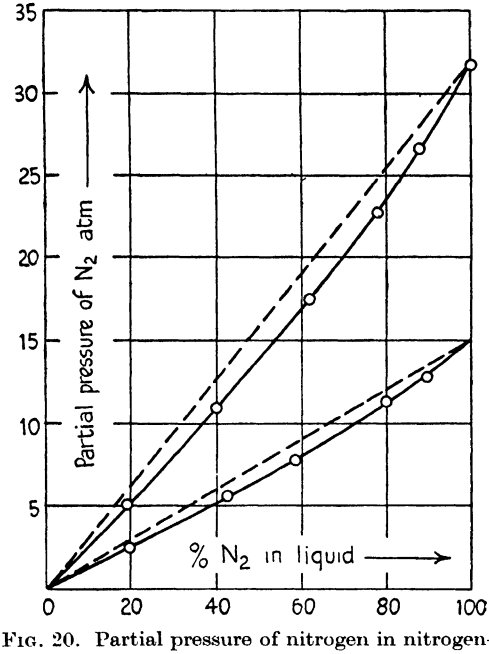


FIG. 20. Partial pressure of nitrogen in nitrogen–oxygen mixtures

accurately by equation (28) up to pressures close to the critical, whereas (26) failed at comparatively low pressures. Fig. 19 shows the fugacity of nitrogen in oxygen–nitrogen mixtures as a function of concentration according to the calculations of Krichevsky and Torocheshnikov. In Fig. 20

the partial pressures are shown to be very far from linear. In the case of oxygen–nitrogen mixtures the experimental data are taken from Dodge and Dunbar's† paper; the nitrogen–carbon monoxide data were from Torocheshnikov's‡ own experiments.

In the case of perfect solutions, all the properties of the mixture can be calculated from data applying to the pure components and can be expressed in simple formulae involving pressure or fugacity, according to whether the vapour phase may or may not be considered as a perfect gas.§

When the vapour is a perfect gas, then, as we have seen, the total pressure is a linear function of the composition of the liquid phase. This means that the boiling-curve of a perfect binary solution in a (p, x) diagram is a straight line. The shape of the dew-curve will be obtained by considering the total pressure p as a function of the composition z of the vapour. From (26) we obtain

$$p = \pi_1 x_1 + \pi_2(1-x_1). \tag{30}$$

Moreover, since (26) requires the vapour to be a perfect gas,

$$p_1 = z_1 p, \qquad p_2 = (1-z_1)p;$$

so with

$$p_1 = x_1 \pi_1, \qquad p_2 = (1-x_1)\pi_2,$$

$$\frac{z_1}{1-z_1} = \frac{x_1}{1-x_1}\frac{\pi_1}{\pi_2}. \tag{31}$$

Solving (31) for x_1 we obtain

$$x_1 = \frac{z_1 \pi_2}{\pi_1 - (\pi_1 - \pi_2)z_1}. \tag{32}$$

Inserting this in (30) we find

$$p = \frac{\pi_1 \pi_2}{\pi_1 - (\pi_1 - \pi_2)z_1}. \tag{33}$$

The curve depicting pressure as a function of the composition of the vapour phase, i.e. the dew-curve, is therefore part of a hyperbola. The (p, x) diagram of a perfect solution, the vapour of which is a perfect gas, is thus shaped as in Fig. 21, and may be quantitatively deduced if the vapour pressures of the two components are known at the temperature concerned.

In order to deduce the (T, x) diagram of a perfect solution, again

† B. F. Dodge and A. Dunbar, *J. Amer. Chem. Soc.* **49**, 591 (1927).

‡ N. Yushkevich and N. Torocheshnikov, *Zhurnal khimicheskoi Promyshlennosti*, **13**, No. 21 (1936).

§ See H. Hausen, 'Materialtrennung durch Destillation und Rektifikation', *Der Chemie-Ingenieur*, I, part 3, ch. 15, p. 70 et seq. (Leipzig, 1933).

assuming the vapour to be a perfect gas, we may solve (30) and (33) for x_1 and z_1 respectively, obtaining

$$x_1 = \frac{p-\pi_2}{\pi_1-\pi_2} \tag{34}$$

and

$$z_1 = \pi_1 x_1/p. \tag{35}$$

If we know π_1 and π_2 as functions of T we can calculate the (T,x) curves for constant p.

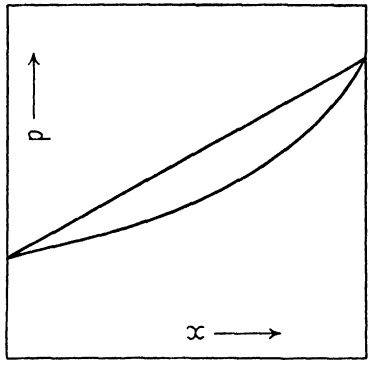


FIG. 21. (p,x) curves of perfect solution

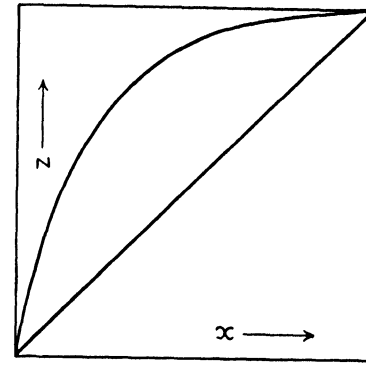


FIG. 22. Concentration curve of perfect solution

x concentration of more volatile component in liquid; z concentration of more volatile component in vapour. The diagonal is shown for comparison

Finally, we can obtain the *concentration curve* z_1 as a function of x_1 from equation (31), which gives

$$z_1 = \frac{\pi_1 x_1}{\pi_2+(\pi_1-\pi_2)x_1}, \tag{36}$$

or, if $\pi_1/\pi_2 = \epsilon$,

$$z_1 = \frac{\epsilon x_1}{1+(\epsilon-1)x_1}. \tag{37}$$

This curve is of the type shown in Fig. 22. The greater ϵ, the more it differs from the diagonal. If, in the interval of temperature concerned, ϵ may be considered as constant, the curve is a hyperbola.

In the case of ternary mixtures, the problem is to find the dew- and boiling-curves at constant T and p which describe the states the system passes through when one of the components is varied. Let the concentrations of the liquid be x_1, x_2, x_3, and those of the vapour phase be z_1, z_2, z_3, and suppose z_1 to be arbitrarily chosen and varied. When the

vapour is a perfect gas we may again use

$$p_i = x_i \pi_i. \tag{26}$$

With $$p_i = z_i p \tag{38}$$

this gives $$x_1 = z_1 p/\pi_1. \tag{39}$$

From (26) we obtain $$p = \sum_i x_i \pi_i, \tag{30}$$

from which x_3 may be eliminated with the relation $\sum_i x_i = 1$. This gives

$$x_2 = \frac{p - \pi_3 + x_1(\pi_3 - \pi_1)}{\pi_2 - \pi_3}. \tag{40}$$

Finally, from (26) and (38),

$$z_2 = z_1 x_2 \pi_2 / x_1 \pi_1. \tag{41}$$

Equations (39), (40), and (41), together with the relations

$$x_3 = 1 - x_1 - x_2 \quad \text{and} \quad z_3 = 1 - z_1 - z_2,$$

enable us to compute all the concentrations in both phases as functions of z_1 when the vapour pressures of the pure components are known at the temperature in question. For perfect solutions the series of triangles describing equilibrium at various temperatures and pressures can thus be deduced.

To obtain Hausen's triangles for variable temperature, with their two systems of coordinates, we have only to solve (39) for z_1 and the corresponding equation for z_2 and insert the value of p from (30). If we put $\pi_1/\pi_3 = \epsilon_1$ and $\pi_2/\pi_3 = \epsilon_2$ we obtain the two equations

$$z_1 = \frac{\epsilon_1 x_1}{1 + (\epsilon_1 - 1)x_1 + (\epsilon_2 - 1)x_2}, \qquad z_2 = \frac{\epsilon_2 x_2}{1 + (\epsilon_1 - 1)x_1 + (\epsilon_2 - 1)x_2}, \tag{42}$$

which enable us everywhere to compute x_1, x_2, x_3 when z_1, z_2, z_3 are given. For these perfect solutions the coordinates $x_1 = \text{const.}$ and $x_2 = \text{const.}$ are evidently straight lines.

(f) Multicomponent mixtures—the equilibrium ratio K

The relation between the concentrations x_i and z_i of a component i in the liquid and gaseous phases of a mixture is frequently written in the form

$$z_i = K_i x_i \tag{43}$$

quite irrespective of whether (27) or (29) hold. The factor K_i, which is known as the *equilibrium ratio*, is taken to be a property of the ith component alone, to be a function of temperature and pressure, and to be independent of concentration and of the nature of other components in the mixture. All this is, of course, true by definition in the case of the terms π_i/p in (27) and f_i^0/f in (29). K_i can be determined by direct

experiment or calculated with the help of (24) or with some other semi-empirical relationship.

In general, of course, the relation between vapour and liquid concentration of a component in a mixture cannot be independent of the other components of the mixture, but equation (43) is used mainly in dealing with multi-component mixtures of hydrocarbons as they occur in the oil industry. These approximate closely to perfect solutions for which (29) has been found to hold with fair accuracy, and the use of 'K-charts' has made it possible to develop methods of calculating fractionating plant for hydrocarbon mixtures containing a large number of components. Such charts have been prepared by Sherwood† and others for most of the lower hydrocarbons and some work has been done, especially by Hadden,‡ to ascertain the deviations in the behaviour of certain hydrocarbons from equation (43). K-values have been determined for methane in binary solution with a number of other hydrocarbons, and separate charts have been drawn up for the different cases.

For the simple case of binary perfect solutions, the equilibrium curves can be constructed from the K-values of the pure components as follows:

For one component $z_1 = K_1 x_1$,

and for the other $(1-z_1) = K_2(1-x_1)$;

whence $z_1 = 1-K_2+K_2 x_1$,

and, by substitution and elimination of z_1,

$$x_1 = \frac{K_2-1}{K_2-K_1} \tag{44}$$

and

$$z_1 = \frac{K_1(K_2-1)}{K_2-K_1}. \tag{45}$$

If K_1 and K_2 are known as functions of temperature and pressure, x_1 and z_1 can be determined from (44) and (45).

4. The determination of equilibrium curves

The experimental material on the equilibrium of binary and ternary mixtures of low-boiling substances is still comparatively scarce and most of it is of very recent date. Even now not nearly all the systems that are important in the separation of gases have been studied.

The reason for this scarcity of data is to be sought in the very considerable experimental difficulties that are incurred when a mixture is

† T. K. Sherwood, *Absorption and Extraction* (McGraw-Hill, 1937), pp. 105–7.

‡ S. T. Hadden, *Chem. Eng. Progress*, **44**, 37, 135 (1948).

to be brought to exact equilibrium under well-defined conditions of pressure and temperature. The determinations that have to be made in studying equilibria are those of pressure, temperature, and composition. Methods for measuring pressure and temperature have been well developed long ago, and here we meet with no overwhelming obstacles. Pressures are usually determined with mercury manometers at low and moderate values, and higher pressures are measured with Bourdon gauges. These secondary manometers must be recalibrated frequently with a pressure balance. In accurate experiments it is advisable to employ a pressure balance directly without having recourse to Bourdon gauges at all.

For measuring temperature all the four well-known low-temperature methods have been successfully applied: gas thermometers, vapour-pressure thermometers, thermo-couples, and resistance thermometers. Vapour-pressure and resistance thermometers are probably the best suited for this purpose.

The composition of the mixture is generally determined by the classical methods of gas analysis. These are mostly cumbersome and require a considerable time for each test. The measurements are thus greatly protracted, since it is usually necessary to analyse a number of mixtures in each experiment. There are two ways out of this difficulty: firstly, methods of determining equilibrium can be devised in which no analyses need be made; secondly, physical methods may be employed to analyse the mixtures. These methods, though they often require rather a complicated equipment, are mostly more accurate than chemical determinations and require less time. In some cases it is possible to analyse a stream of gas continuously, which greatly increases the accuracy of the results and considerably shortens the time needed to perform the experiment.

The accurate and swift determination of gas composition is only one of the difficulties encountered in these experiments. The second and more serious problem consists in bringing a mixture to a state of actual phase equilibrium. Unless very great precautions are taken a liquid and a gaseous mixture under fixed conditions of pressure and temperature will remain for long periods of time in a state more or less removed from true equilibrium. This is mainly due to the low coefficients of diffusion and heat transfer and to the fact that small drops of liquid are frequently present in the gaseous phase, whereas they are not noticeable as such in the analysis. As a result, the compositions of gas and liquid actually determined differ from each other less than under

real equilibrium conditions. The inhomogeneous regions thus appear narrower than they should.

A number of 'simplified' methods of determining liquid–vapour equilibrium have been put forward from time to time, but they have almost all had to be discarded in favour of more cumbersome methods, as the results were not sufficiently accurate.

The methods for investigating liquid–vapour equilibrium can be divided roughly into the following groups.

1. **Dew- and boiling-point method.** A gas of known composition is introduced into an equilibrium vessel at constant temperature. The *pressure* is observed at which condensation commences and is completed.

This method was developed by Kuenen at Leiden and has been frequently employed. It was used by Holst and Hamburger† on argon–nitrogen mixtures, by Bourbo and Ischkin‡ on mixtures of argon and oxygen, and by Steckel§ on nitrogen–carbon monoxide mixtures. It has been developed to considerable perfection by Sage and Lacey,‖ who used it for mixtures of light hydrocarbons, chiefly above room temperature. The method has the advantage that the phases need not be analysed, since the mixtures may be composed arbitrarily, but it must be applied with great care if accurate results are to be obtained.

2. **Static method.** A mixture is confined in the equilibrium vessel at constant temperature and pressure corresponding to a point in the inhomogeneous region of the phase diagram. The *composition* of the liquid and vapour phases is determined.

The static method was used by Verschoyle†† on nitrogen–hydrogen, carbon monoxide–hydrogen, and the ternary system nitrogen–carbon monoxide–hydrogen, by Freeth and Verschoyle‡‡ for hydrogen–methane mixtures, and by Fedoritenko and Ruhemann§§ for mixtures of nitrogen and helium.

It is a useful and fairly accurate method for high and moderate pressures, especially when the temperature is above the critical point of one of the components. Its chief disadvantage is that equilibrium is apt to be destroyed when analysis tests are taken. It is this that renders the method inaccurate at low pressures, since here the amount

† G. Holst and L. Hamburger, *Zeitschr. f. phys. Chemie*, **91**, 513 (1916).
‡ P. Bourbo and I. Ischkin, *Phys. Zeitschr. d. Sowjetunion*, **10**, 271 (1936).
§ F. Steckel, ibid. **8**, 337 (1935).
‖ B. H. Sage and W. N. Lacey, *Ind. Eng. Chemistry*, **26**, 103, 214 (1934).
†† T. T. H. Verschoyle, *Trans. Roy. Soc.* (A), **230**, 189 (1931).
‡‡ F. A. Freeth and T. T. H. Verschoyle, *Proc. Roy. Soc.* (A), **130**, 453 (1931).
§§ A. Fedoritenko and M. Ruhemann, *Techn. Phys. of U.S.S.R.* **4**, 1 (1937).

of gas needed for the analysis is of the order of magnitude of the total quantity of gaseous phase present in the equilibrium vessel.

3. **Flow method.** The mixture is passed slowly and continuously at constant pressure through an apparatus that is constructed so as to ensure good thermal contact with the liquid in the cryostat. The gaseous phase flows into a gasometer, the liquid collecting in a receptacle below the equilibrium apparatus. The gas in the gasometer is *analysed* at the end of the experiment as well as a portion of the liquid phase. In some cases gas and liquid are analysed continuously during the run.

The method has been used by Steckel and Zinn† with the system hydrogen–nitrogen–methane, by Ruhemann and Zinn‡ with hydrogen–nitrogen–carbon monoxide, by Fedoritenko and Ruhemann§ with nitrogen and helium, by Ruhemann|| for mixtures of CH_4 and C_2H_6, by Guter, Newitt, and Ruhemann†† for CH_4—C_2H_4 mixtures, and by Atack, Evans, and MacCormack‡‡ for the system C_2H_4—C_3H_8. If properly handled it is reliable and gives quite accurate results. It is suitable for high and medium pressures, but is not very good in the critical region. There is a considerable danger of the equilibrium vessel becoming swamped, owing to too rapid condensation.

4. **Circulation method.** A gaseous mixture is circulated through the liquid in the equilibrium vessel by a small pump at constant pressure and temperature. In course of time liquid and gas assume equilibrium. Both phases are *analysed* from time to time until the analysis tests give constant results.

This method was developed by Dodge and Dunbar§§ in their work on oxygen–nitrogen mixtures. It has been employed by Torocheshnikov|||| in studying the equilibrium of the carbon monoxide–nitrogen system. It is probably the most accurate and reliable of all existing methods but demands a rather elaborate and complicated equipment.

Fig. 23 shows the apparatus of type (1) used by Bourbo and Ischkin for studying mixtures of oxygen and argon at low pressures. The mixture of known composition is transmitted from the cylinder 6 through the valve 7 to the glass equilibrium vessel 8 of about 8 c.c.

† F. Steckel and N. Zinn, *Zhurnal khimicheskoi Promyshlennosti*, **16**, No. 8 (1939).
‡ M. Ruhemann and N. Zinn, *Phys. Zeitschr. d. Sowjetunion*, **12**, 389 (1937).
§ A. Fedoritenko and M. Ruhemann, *Techn. Phys. of U.S.S.R.* **4**, 1 (1937).
|| M. Ruhemann, *Proc. Roy. Soc.* (A), **171**, 121 (1939).
†† M. Guter, D. M. Newitt, and M. Ruhemann, ib. (A), **176**, 140, 1940.
‡‡ D. Atack, M. G. Evans, and K. E. MacCormack, in the press.
§§ B. F. Dodge and A. Dunbar, *J. Amer. Chem. Soc.* **49**, 591 (1927).
|||| N. Torocheshnikov, *Journ. Techn. Phys.* (Russian), **7**, 1107 (1937).

capacity, immersed in the cryostat 9, which is filled with liquid oxygen. The cryostat is a copper Dewar vessel of 2 litres capacity and is fitted with a mechanical stirrer 18. The temperature in the cryostat is read with an oxygen vapour-pressure thermometer 1 on a mercury mano-

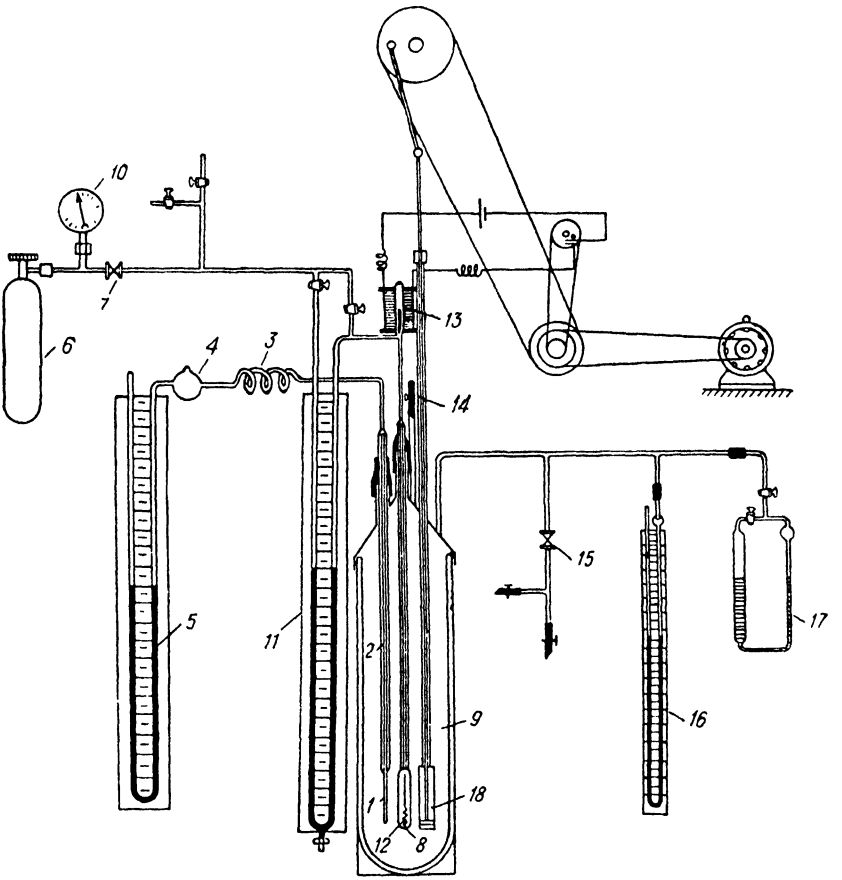


FIG. 23. Apparatus for boiling-point method†

meter 5. 1 is placed immediately beside 8 and the tube 2 connecting it to 5 is insulated from the liquid in the cryostat, as a vertical temperature head in the cryostat would influence the readings of the thermometer. The temperature in the cryostat is adjusted by pumping off the vapour and regulating valve 15 with the help of a mercury manometer 16 and a differential manometer 17 filled with a light oil. The equilibrium vessel is equipped with a light stirrer 12 operated with an

† P. Bourbo and I. Ischkin, *Phys. Zeitschr. d. Sowjetunion*, **10**, 271 (1936).

electromagnet 13. The pressure in the equilibrium vessel is read on the mercury manometer 11.

In the experiments of Bourbo and Ischkin only the boiling-points were determined, i.e. the pressures at which mixtures of different concentrations completely condensed. The corresponding dew-curves were computed by solving the Duhem–Margules equation.

Fig. 24 gives a sketch of an apparatus of the same type (1) used by Steckel on nitrogen–carbon monoxide mixtures at pressures up to

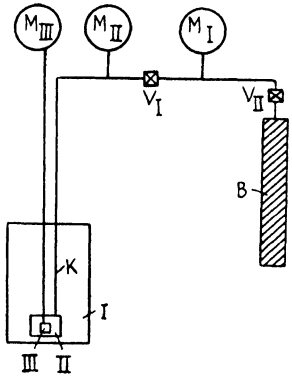


FIG. 24. Arrangement for dew- and boiling-point method

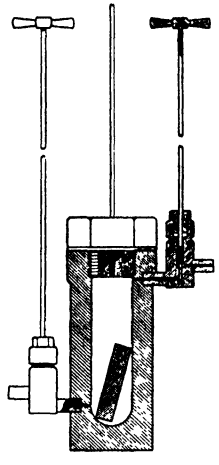


FIG. 25. Equilibrium vessel for static method

17 atm. The copper equilibrium vessel II is fitted with a vapour-pressure thermometer III and suspended from a German silver capillary K in a copper cryostat I, the temperature of which can be varied as in the apparatus just described. A steel cylinder B containing the mixture of known composition is connected with II through valves V_I and V_{II}, separated by a narrow tube and a Bourdon gauge M_I. The pressure in II is read on M_{II}. The space between V_I and V_{II} is filled with gas at the pressure of the cylinder and is then transferred in small portions through V_I to the equilibrium vessel, V_{II} being closed. M_{II} is read as a function of M_I. As the volume between V_I and V_{II} consists mainly of M_I itself, the readings of M_I are a sensitive measure of the volume of gas passed into II. As long as no condensation occurs, a straight line is obtained by plotting the readings of M_{II} against those of M_I. At the dew-point this line shows a marked kink, since the condensation retards the rise of pressure in II. When II is completely filled with liquid another still more pronounced kink is observed as the pressure in II now rises rapidly

when small portions of gas are added owing to the small compressibility of the liquid.

This apparatus is exceedingly simple but not very reliable, as one can never be quite certain that equilibrium in II has actually been attained.

Fig. 25 shows the equilibrium vessel used by Verschoyle for his static method (2), in studying the equilibrium of hydrogen–nitrogen–carbon monoxide at pressures up to 225 atm. The vessel is of brass and has a volume of 9 c.c. The mixture is admitted through the central capillary tube. The analysis tests are taken through the two lateral outlets, fitted with specially constructed taps that work at low temperatures. The spindles of the taps extend through the cover of the cryostat, so that they may be operated at room-temperature.

In Fig. 26 a sketch is given of the apparatus constructed by Steckel and Zinn according to the flow method (3), and used up to 100 atm. in studying mixtures of hydrogen, nitrogen, and methane. A similar apparatus was used by Guter, Newitt, and Ruhemann for investigating methane–ethane and methane–ethylene mixtures and mixtures of methane–ethylene–ethane. The mixture is passed very slowly through a bundle of copper capillary tubes of 2 mm. outer diameter and 1 mm. inner diameter, which are immersed in the cryostat. The liquid–gaseous mixture, which is formed in the capillaries, enters the receiver, the liquid collecting in the conical bottom of the vessel, and the gas passing out through the tube T_2. The mixture entering the receiver is directed so as to strike the walls, thus increasing the surface of contact and giving the liquid a good chance of trickling down into the base. A piece of copper wire gauze G is placed below the exit at the top of the

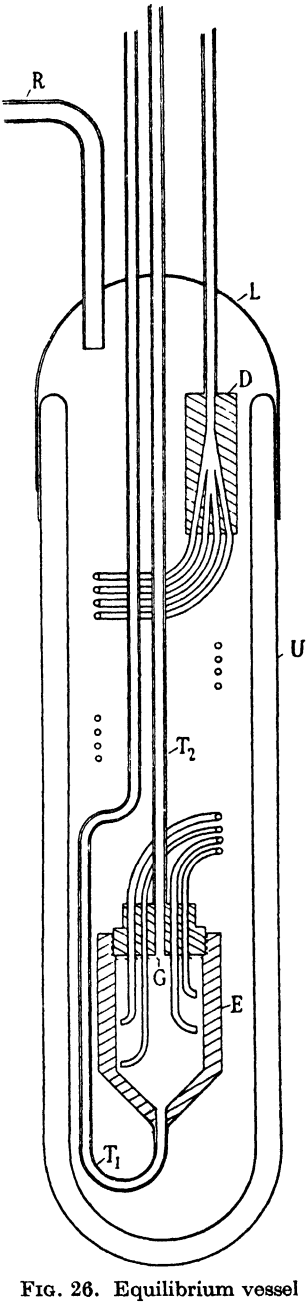


FIG. 26. Equilibrium vessel and cryostat for flow method

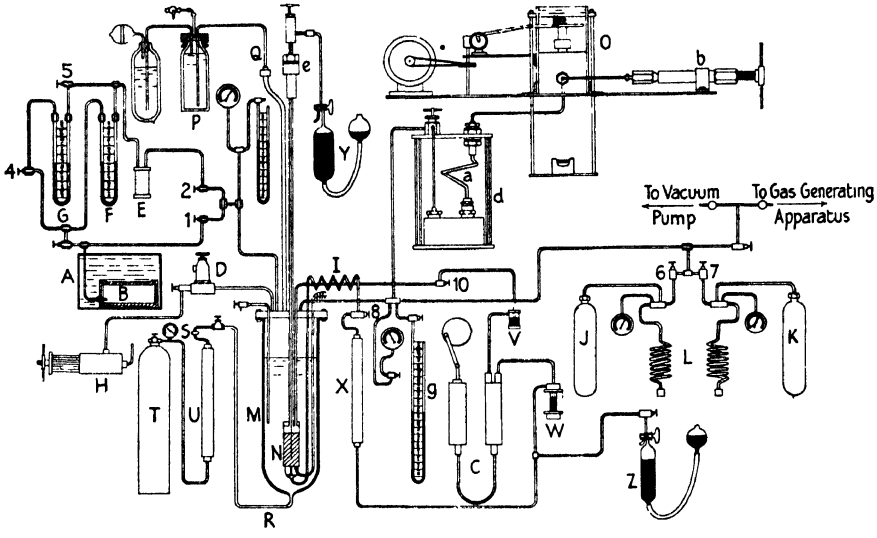


FIG. 27. Apparatus for circulation method

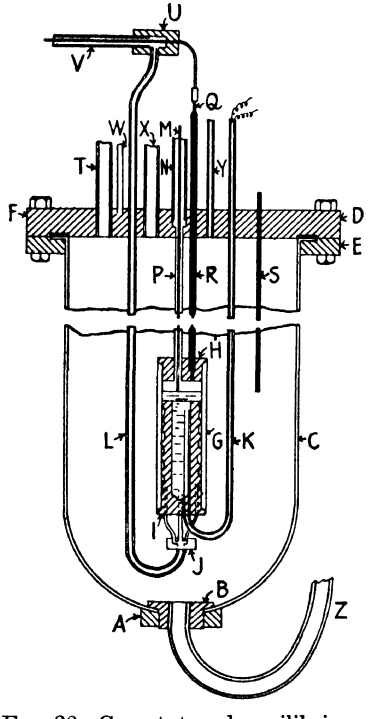


FIG. 28. Cryostat and equilibrium vessel for circulation method

receiver to catch any drops of liquid that may be carried away by the vapour. During the run the pressure is maintained constant, the liquid gradually collecting. The vapour phase is passed out continuously through a valve, which is connected to the gasometer when it may be assumed that a stationary state has been reached. The analysis test of the liquid is taken through a valve attached to T_1 at the end of the run, the pressure being maintained constant during the operation.

Fig. 27 shows the equipment used by Dodge and Dunbar† on oxygen–nitrogen mixtures. The circulation method (4) was used. By means of the mercury-column circulating-pump C vapour is taken from the equilibrium chamber N through a heat-exchanger I, a valve W, a reservoir X, and back to N again. In the figure J and K are storage cylinders for oxygen and nitrogen; O is a piston pressure balance with an equilibrium indicator d; Y and Z are mercury burettes to enable samples of liquid and vapour to be taken. Liquid oxygen for the bath is forced out of the metal vacuum vessel P into the cryostat M, where its temperature is kept constant by means of an 'artificial atmosphere' maintained in the cylinder B and regulated with the plunger valve H and the differential manometers F and G, filled with mercury and oil respectively. The cryostat and equilibrium vessel are shown separately in Fig. 28. Gas is admitted through the tube L and the manifold J, which conducts it in three separate currents to three threads, cut on the outside of the copper piece I inside the brass tube G. This arrangement ensures adequate mixing of vapour and liquid.

5. Survey of experimental results

The following figures show the equilibrium curves of those binary and ternary mixtures that have been investigated up to date, the components of which are gaseous at room temperature and atmospheric pressure. Where possible (p, x) and (T, x) curves are shown. Authors' names and references are given and the type of apparatus is mentioned with which the experiments were carried out.

† B. F. Dodge and A. K. Dunbar, *Journ. Amer. Chem. Soc.* **49**, 591 (1927).

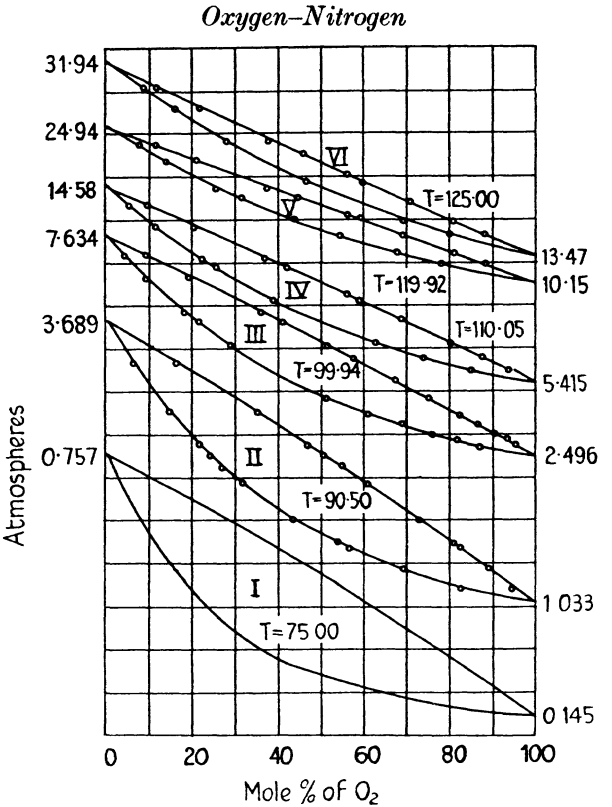


FIG. 29. (p, x) curves at 75·00, 90·50, 99·94, 110·05, 119·92, and 125·00° K. Dodge and Dunbar, 'Circulation Method', *Journ. Amer. Chem. Soc.* **49**, 591 (1927)

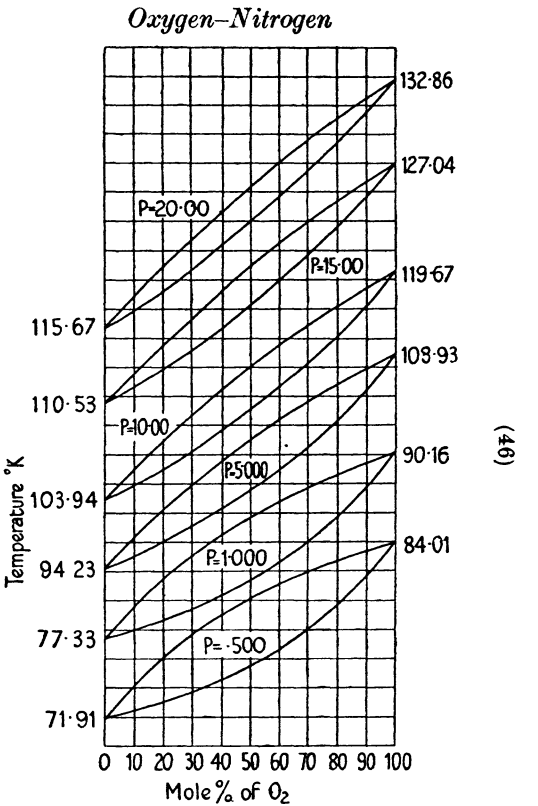


FIG. 30. (T, x) curves at 0·5, 1, 5, 10, 15, and 20 atm. Dodge and Dunbar, 'Circulation Method' (see Fig. 29)

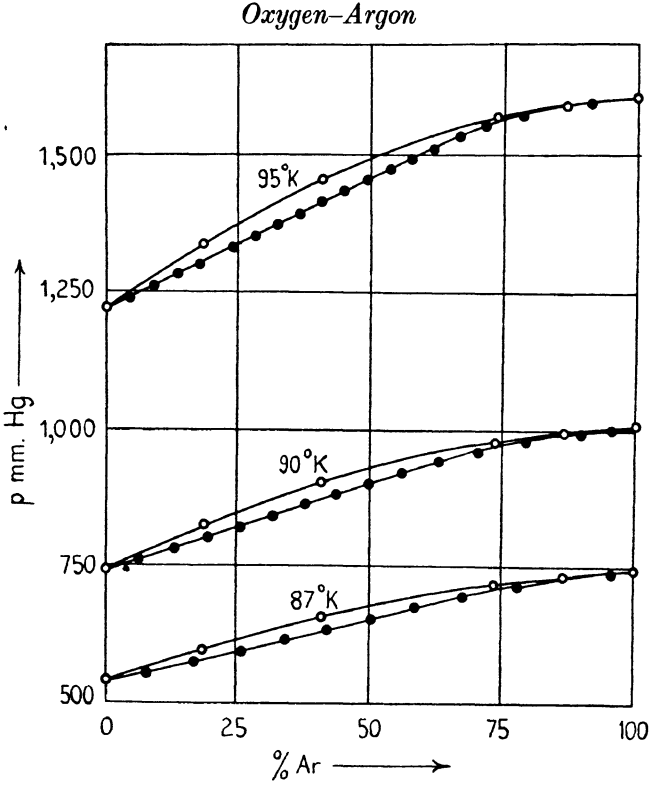


FIG. 31. (p, x) curves at 87, 90, and 95° K. Bourbo and Ischkin, 'Boiling-point Method', *Phys. Zeitschr. d. Sowjetunion*, **10**, 271 (1936)

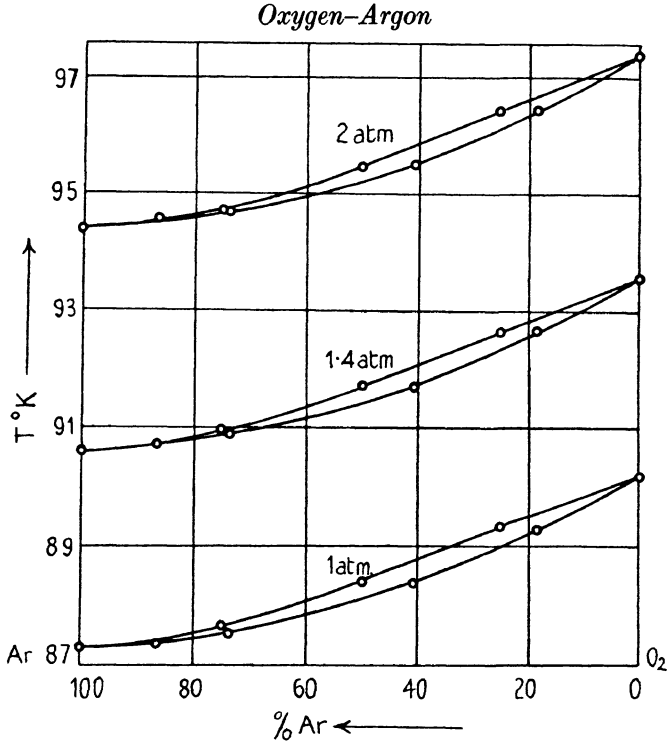


FIG. 32. (T, x) curves at 1, 1·4, and 2 atm. Bourbo and Ischkin, 'Boiling-point Method' (see Fig. 31)

Argon–Nitrogen

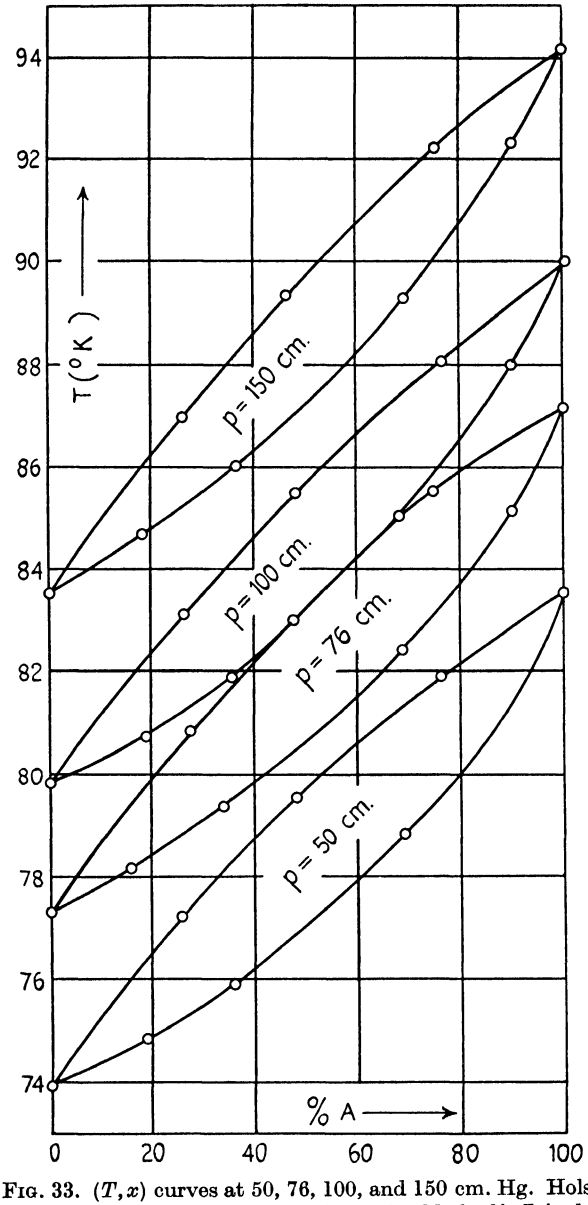


FIG. 33. (T, x) curves at 50, 76, 100, and 150 cm. Hg. Holst and Hamburger, 'Dew- and Boiling-point Method', *Zeitschr. f. phys. Chem.* **91**, 513 (1916)

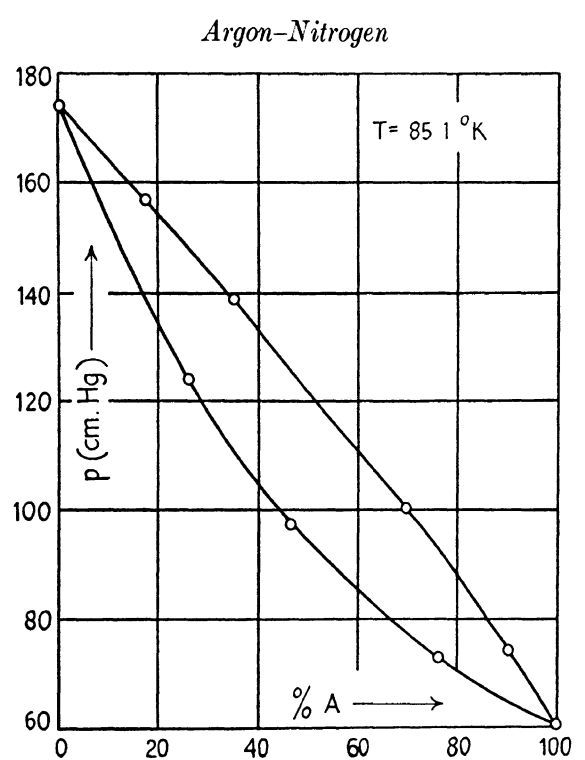


FIG. 34. (p, x) curve at 85° C. Holst and Hamburger, 'Dew- and Boiling-point Method' (see Fig. 33)

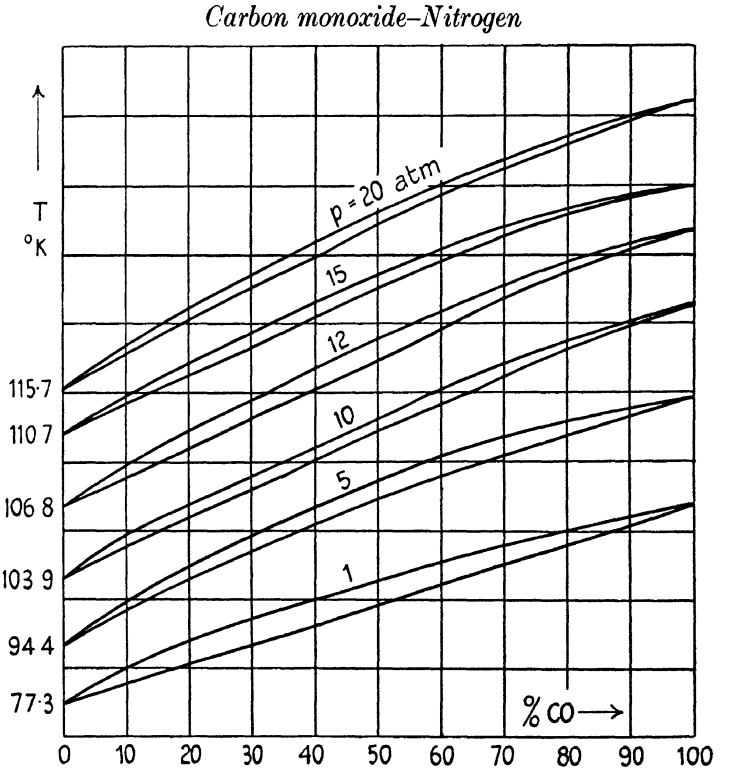


FIG. 35. (T, x) curves at 1, 5, 10, 12, 15, and 20 atm. Yushkevich and Torocheshnikov, 'Circulation Method', *Zhurn. khim. Prom.* **13**, No. 21, p. 1273 (1936)

Carbon monoxide–Nitrogen

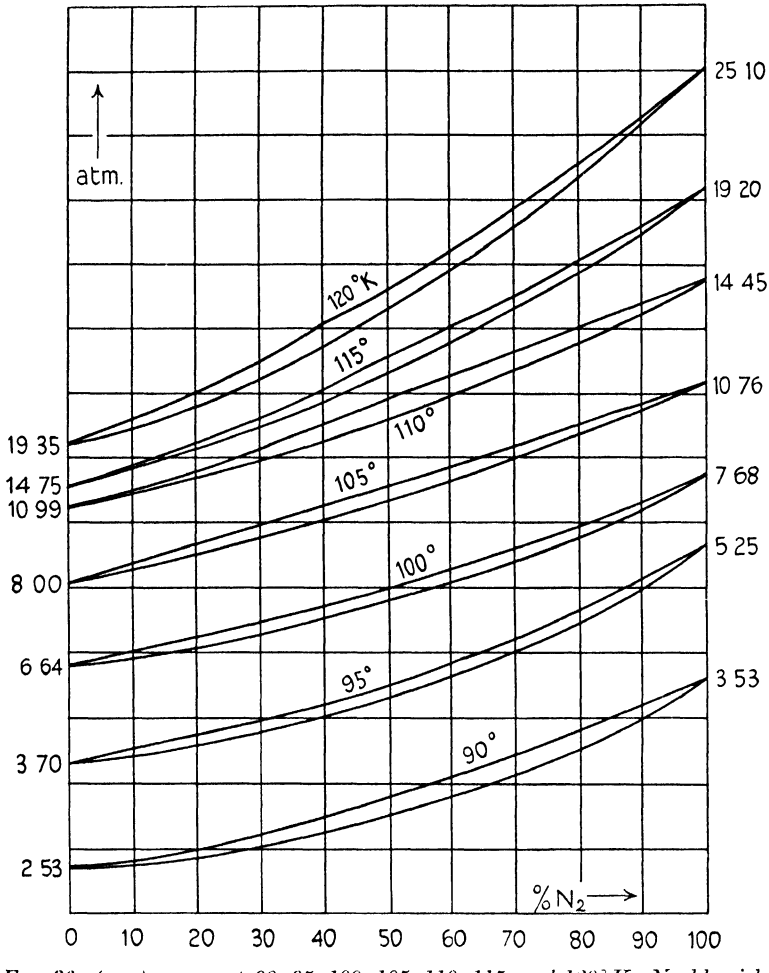


FIG. 36. (p, x) curves at 90, 95, 100, 105, 110, 115, and 120° K. Yushkevich and Torocheshnikov, 'Circulation Method', *Zhurn. khim. Prom.* **13**, No. 21, p. 1273 (1936)

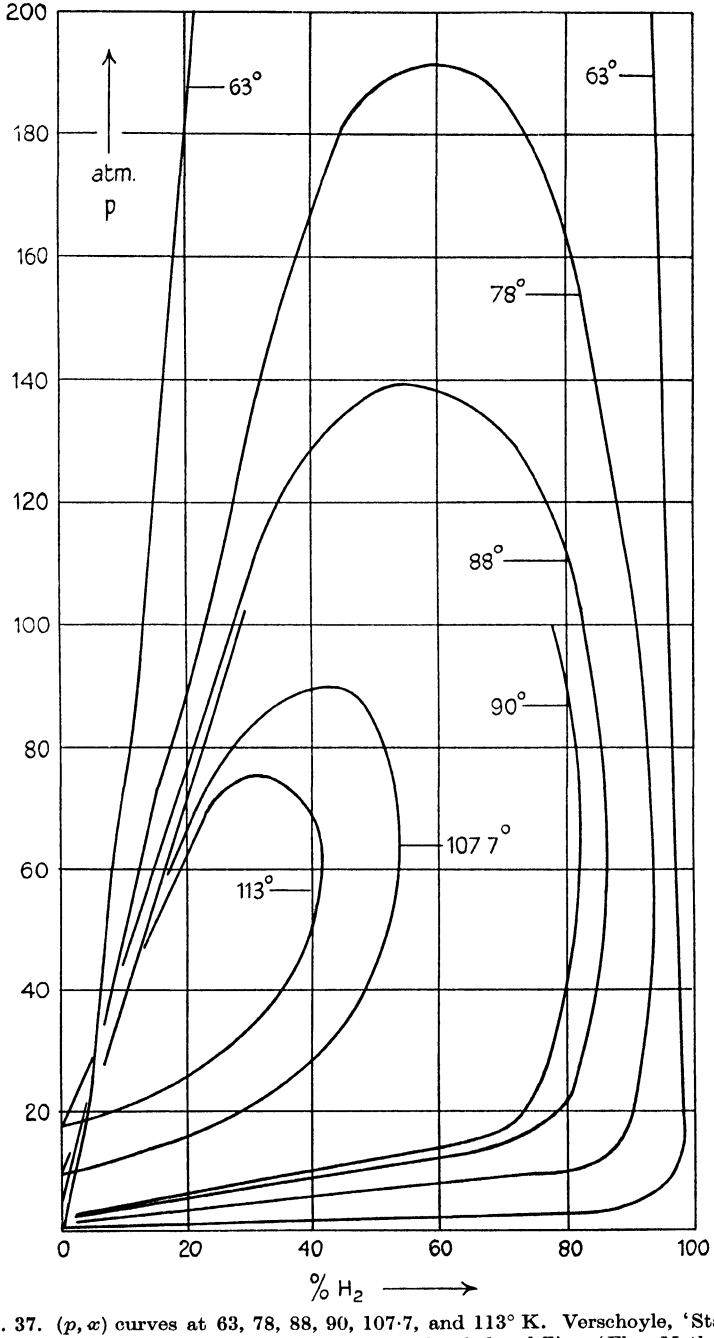


FIG. 37. (p, x) curves at 63, 78, 88, 90, 107·7, and 113° K. Verschoyle, 'Static Method', *Trans. Roy. Soc.* (A), **230**, 189 (1931); Steckel and Zinn, 'Flow Method', *Zhurn. khim. Prom.* **16**, No. 8 (1939); Ruhemann and Zinn, 'Flow Method', *Phys. Zeitschr. d. Sowjetunion*, **12**, 389 (1937)

Carbon monoxide–Nitrogen–Hydrogen

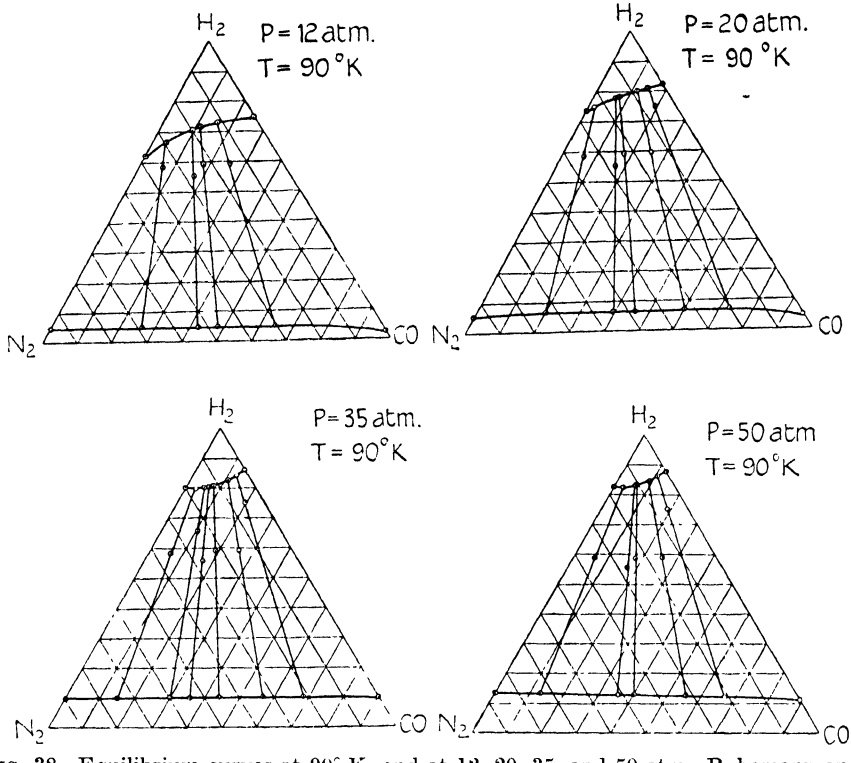


FIG. 38. Equilibrium curves at 90° K. and at 12, 20, 35, and 50 atm. Ruhemann and Zinn, 'Flow Method' (see Fig. 37). Curves also obtained at lower temperatures

Carbon monoxide–Hydrogen

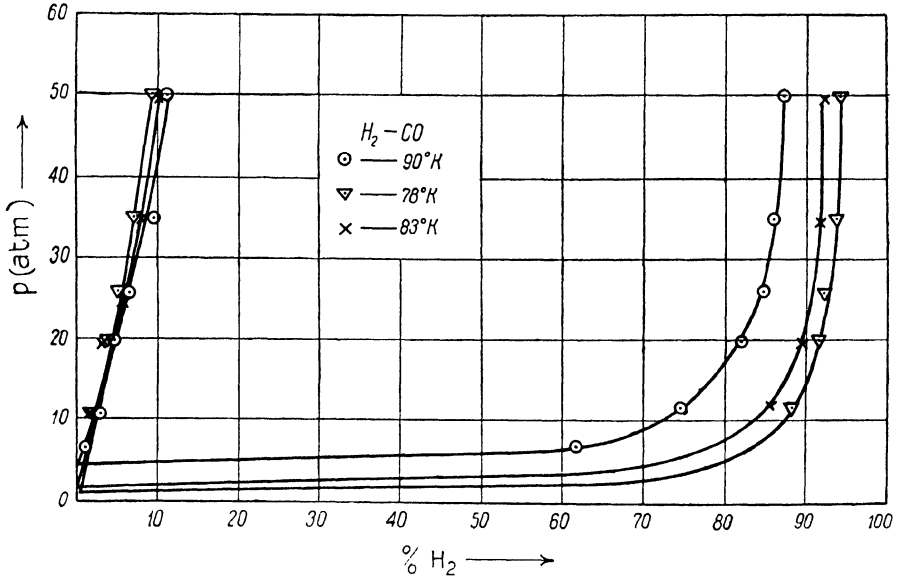


FIG. 39. (p, x) curves at 78, 83, and 90° K. Ruhemann and Zinn, 'Flow Method', *Phys. Zeitschr. d. Sowjetunion*, **12**, 389 (1937)

Methane–Hydrogen

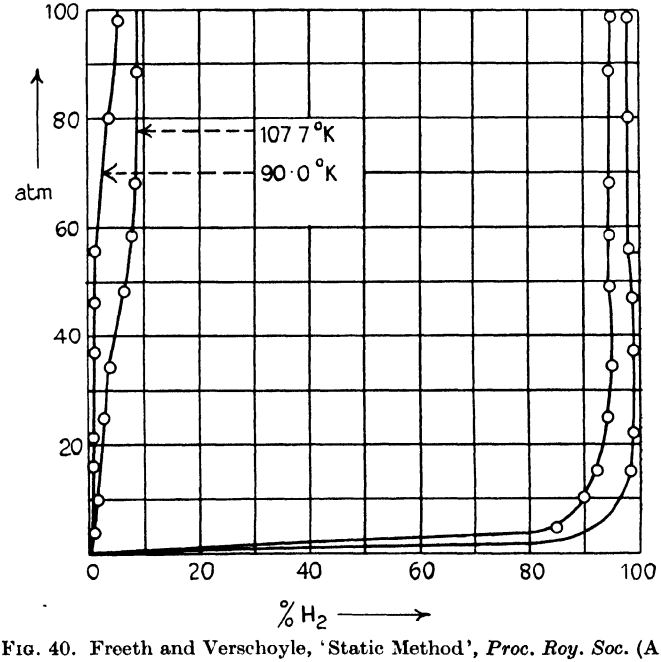


FIG. 40. Freeth and Verschoyle, 'Static Method', *Proc. Roy. Soc.* (A), **130**, 453 (1931); Steckel and Zinn, 'Flow Method' (see Fig. 37)

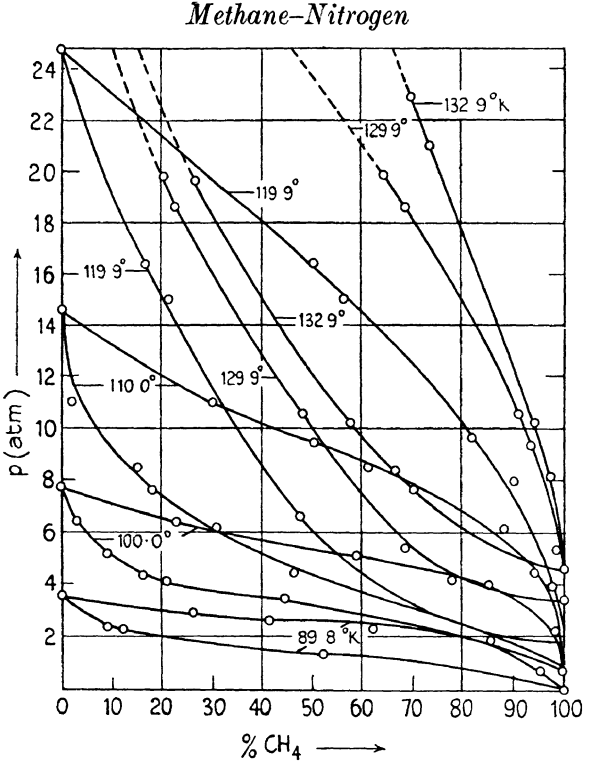


FIG. 41. (p, x) curves at 89·8, 100·0, 110·0, 119·9, 129·9, and 132·9° K. Torocheshnikov and Levius, 'Circulation Method', *Zhurn. khim. Prom.* **16,** No. 1, p. 19 (1939)

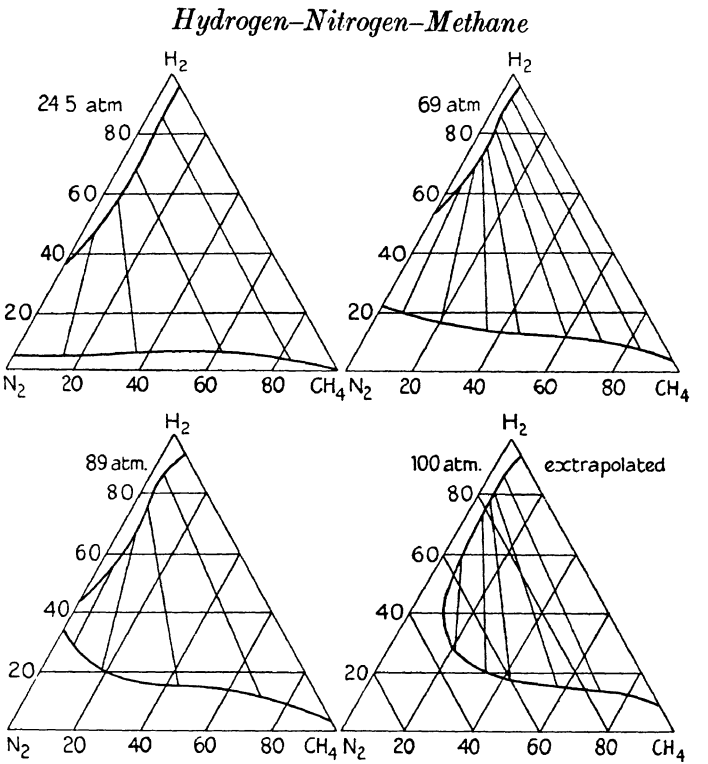
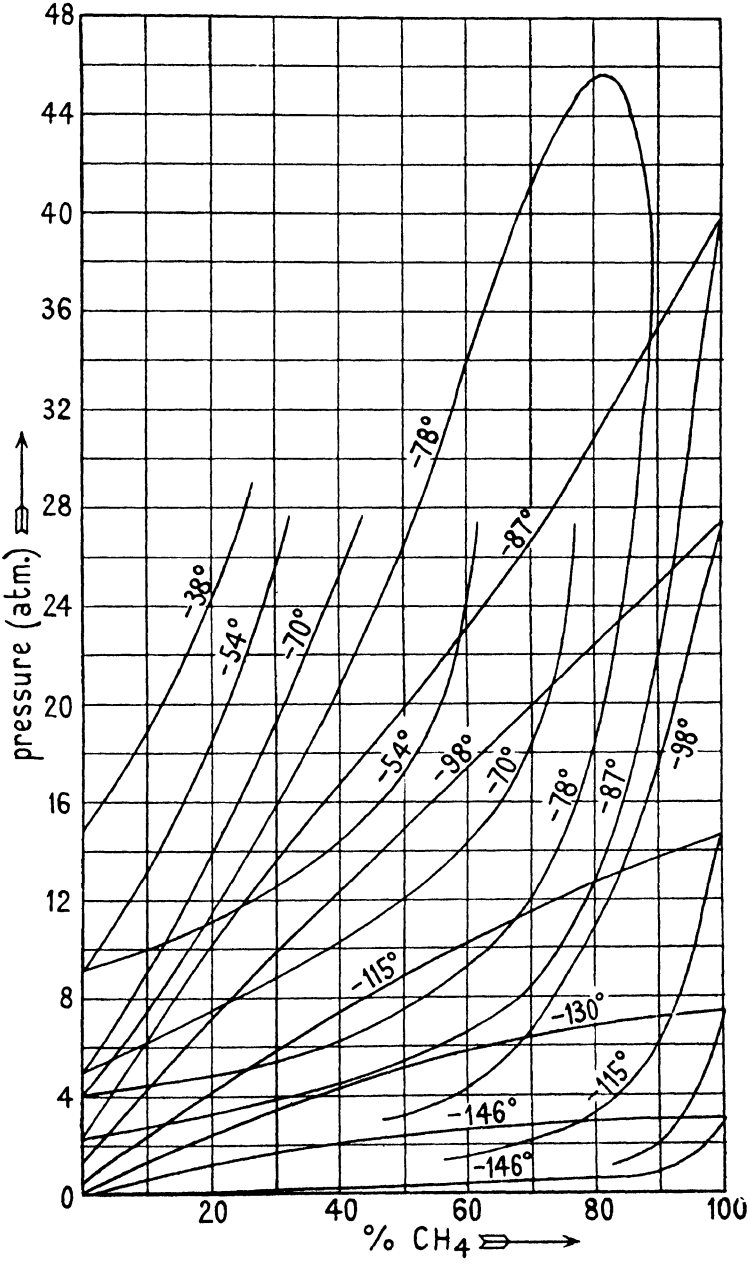


FIG. 42. Dew- and boiling-curves at 107·7° K., at 24·5, 69, and 89 atm., and at 100 atm. extrapolated. Steckel and Zinn, 'Flow Method', *Zhurn. khim. Prom.* **16,** No. 8, p. 24 (1939). (The paper contains further curves at lower and intermediate pressures, as well as a series at 90° K.)

Methane–Ethylene



36500

FIG. 43. (p, x) curves at −146, −130, −115, −98, −87, −78, −70, −54, and −38° C. Guter, Newitt, and Ruhemann, 'Flow Method', *Proc. Roy. Soc.* (A), **176**, 140 (1940); Volova, 'Circulation Method', *Zhurn. fiz. Khim.*, **14**, 268 (1940)

Ethane–Ethylene

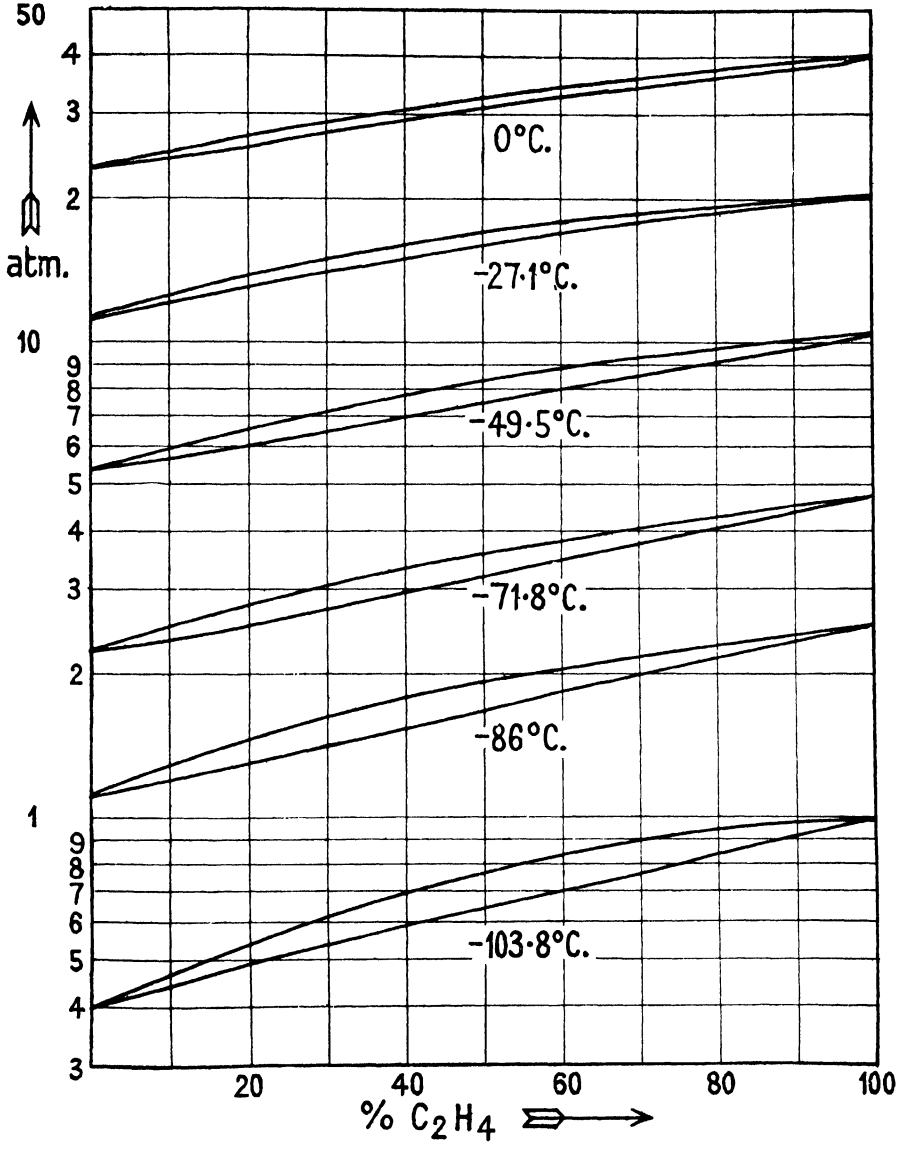


FIG. 44. (p, x) curves at −103·8, −86, −71·8, −49·5, −27·1, and 0° C. Kharakhorin 'Circulation Method', *Zhurn. tekhn. Fiz.* **11**, 1133 (1941). (The paper contains further curves at intermediate temperatures)

Methane–Ethane

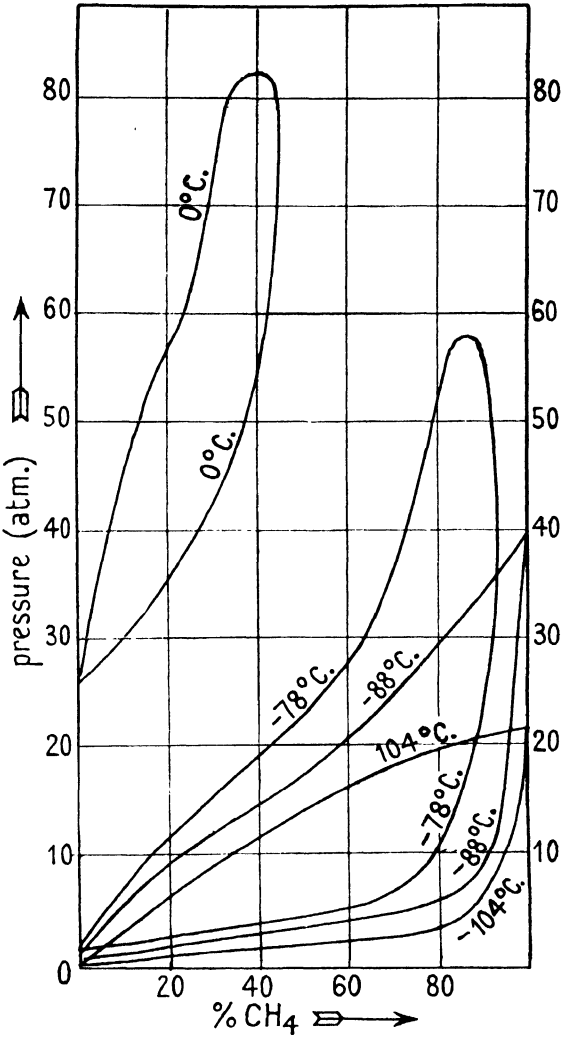


FIG. 45. (p, x) curves at −104, −88, −78, and 0° C. Ruhemann, 'Flow Method', *Proc. Roy. Soc.* (A), **171**, 121 (1939); Guter, Newitt, and Ruhemann, *Proc. Roy. Soc.* (A), **176**, 140 (1940)

Methane–Ethane

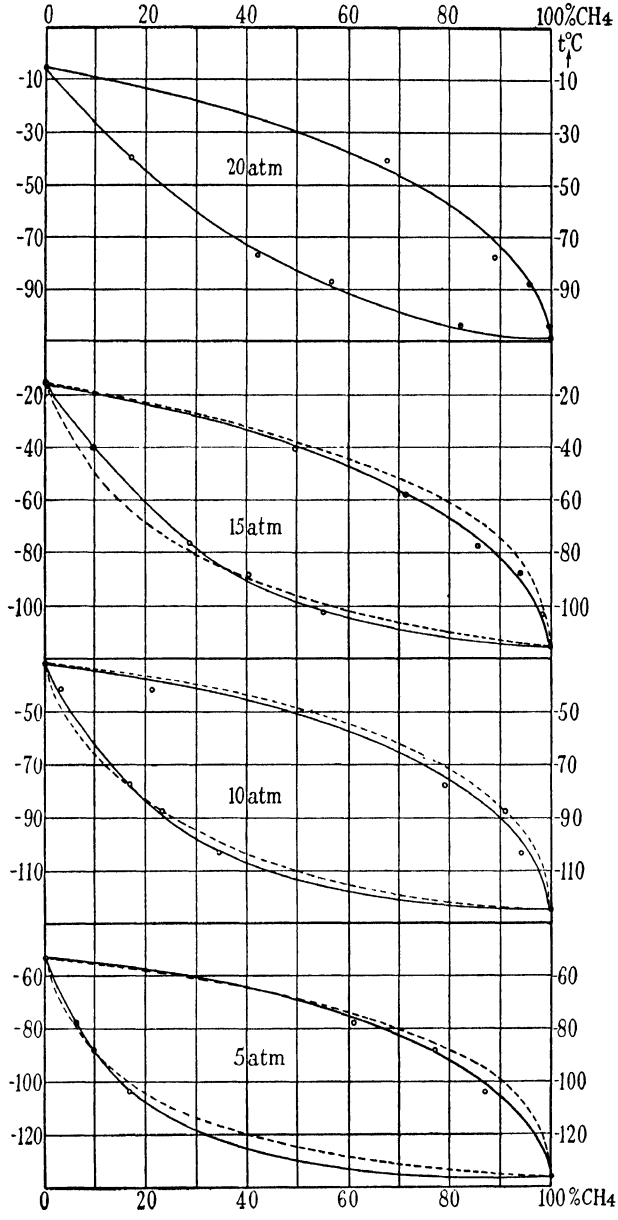


FIG. 46. (T, x) curves at 5, 10, 15, and 20 atm. Ruhemann, 'Flow Method', *Proc. Roy. Soc.* (A), **171**, 121 (1939). (The dotted curves were calculated assuming the mixtures to be perfect solutions)

Methane–Ethylene–Ethane

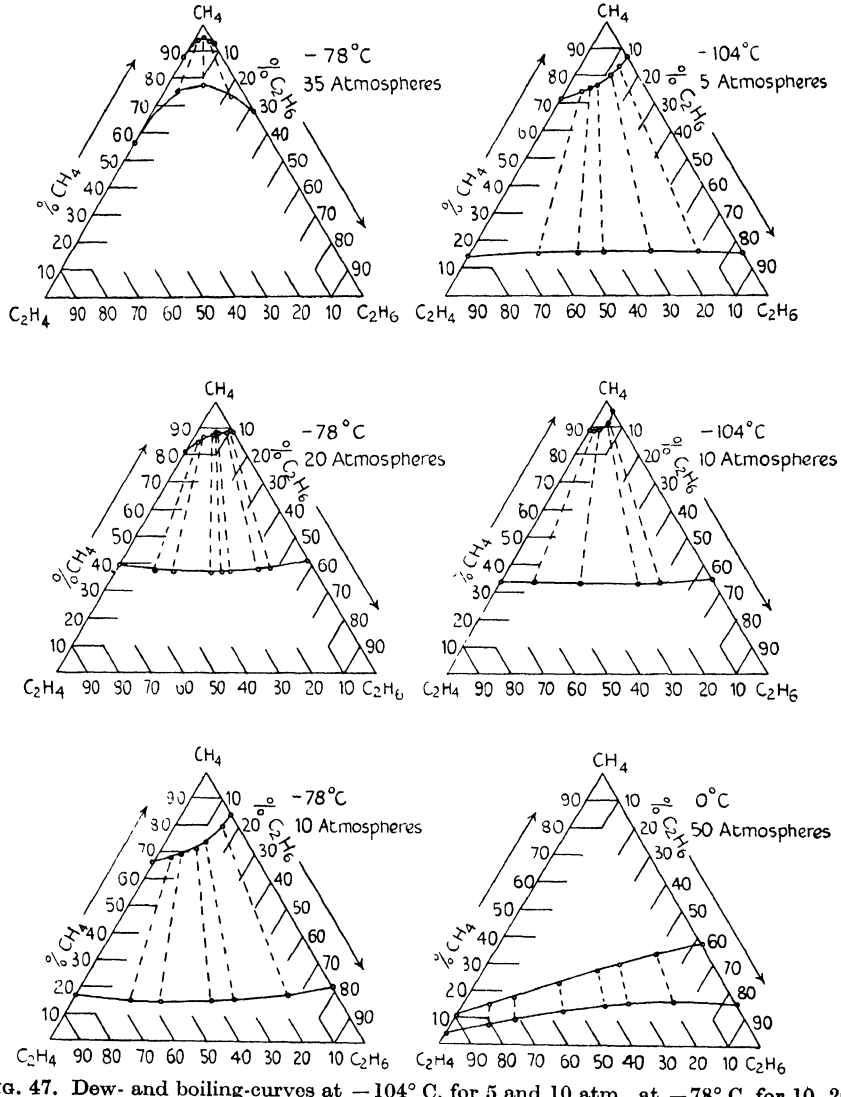


FIG. 47. Dew- and boiling-curves at −104° C. for 5 and 10 atm., at −78° C. for 10, 20, and 35 atm., and at 0° C. for 50 atm. Guter, Newitt, and Ruhemann, 'Flow Method', *Proc. Roy. Soc.* (A), **176**, 140, 1940

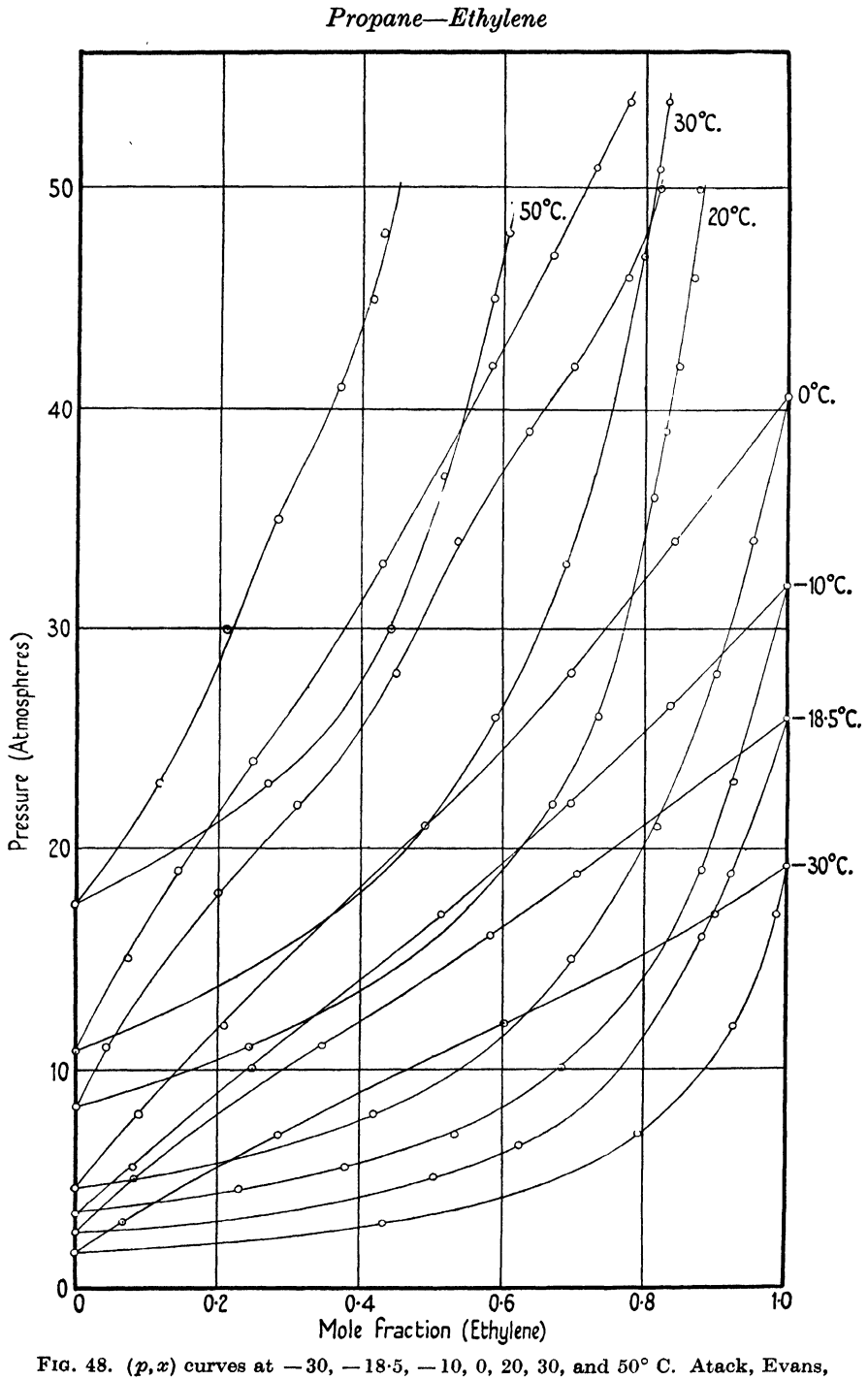


FIG. 48. (p,x) curves at −30, −18·5, −10, 0, 20, 30, and 50° C. Atack, Evans, and MacCormack, 'Flow Method', *Proc. Roy. Soc.* (A) (in the press)

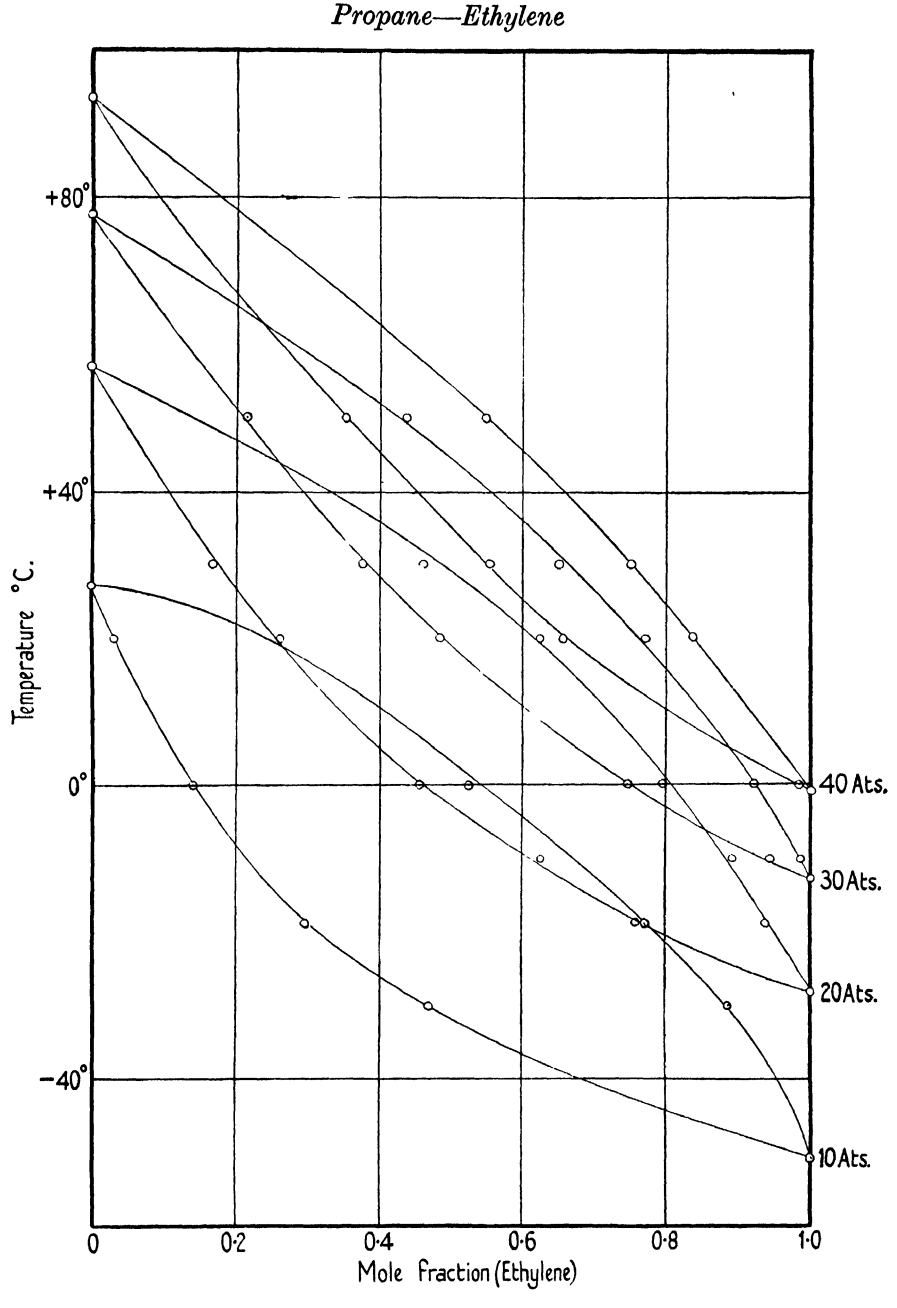


FIG. 49. (T, x) curves at 10, 20, 30, and 40 atm. Atack, Evans, and MacCormack, 'Flow Method', *Proc. Roy. Soc.* (A) (in the press)

Methane–Propane

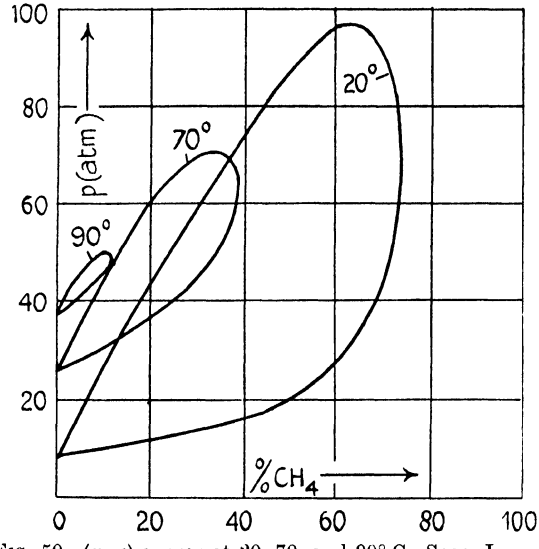


FIG. 50. (p, x) curves at 20, 70, and 90° C. Sage, Lacey, and Schaafsma, 'Dew- and Boiling-point Method', *Ind. Eng. Chem.* **26,** 214 (1934)

Nitrogen–Helium

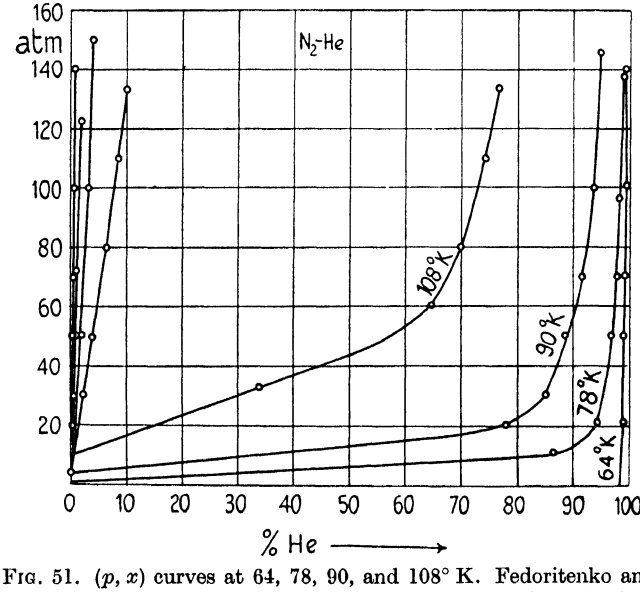
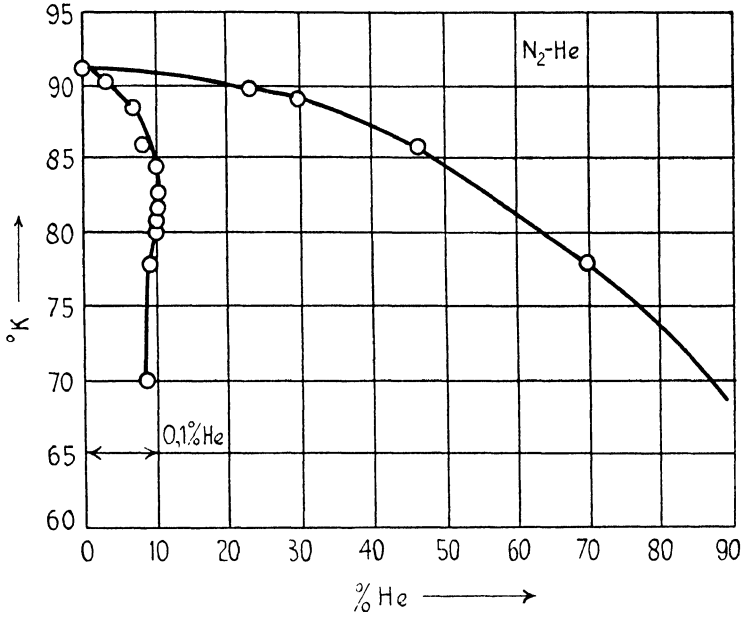
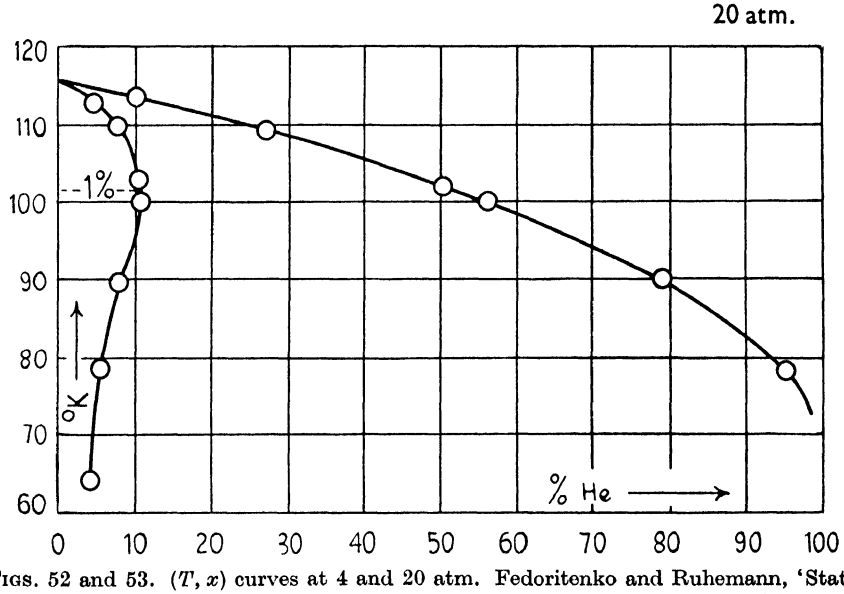


FIG. 51. (p, x) curves at 64, 78, 90, and 108° K. Fedoritenko and Ruhemann, 'Static and Flow Methods', *Techn. Phys. of the U.S.S.R.* **4,** 1 (1937)

Nitrogen–Helium





FIGS. 52 and 53. (T, x) curves at 4 and 20 atm. Fedoritenko and Ruhemann, 'Static and Flow Methods', *Techn. Phys. of the U.S.S.R.* **4**, 1 (1937). The composition scale for the boiling curves has been magnified as indicated

III

THE METHODS OF GAS SEPARATION

1. Condensation and evaporation

CONSIDER a mixture containing 80 per cent. nitrogen and 20 per cent. helium at 20 atm. pressure to be cooled gradually below its point of liquefaction. To see what happens, let us turn to the (T, x) diagram of this mixture in Fig. 53. We note that liquefaction begins at 110·5° K. and that the liquid first condensed contains 99·3 per cent. nitrogen. Thus, even the first drop of condensed liquid is almost pure nitrogen. However, the gaseous phase still contains only 20 per cent. helium. If we now cool the mixture further, we enter the inhomogeneous region. At 108° the liquid is slightly impurer, 99·1 per cent. N_2, but the gas already contains 30 per cent. He, and we find that 37 per cent. of the mixture has been condensed. By lowering the temperature still further, we obtain the figures of Table 8, which show us how the separation proceeds when more and more gas is condensed.

TABLE 8. *Separation of a Helium–Nitrogen Mixture by Simple Condensation at* 20 *atm. Composition of Mixture*: 80 *per cent.* N_2, 20 *per cent.* He

T	x_{N_2}	z_{He}	ϵ
110·5	99·3	20	0
108	99·1	30	0·37
105	99·0	40	0·54
101	99·0	50	0·64
98	99·1	60	0·69
93·5	99·2	70	0·74
89	99·3	80	0·77
82·5	99·4	90	0·79
77	99·6	98	0·80

x_{N_2} = mole per cent. nitrogen in liquid; z_{He} = per cent. helium in gas; ϵ = fraction of mixture condensed.

Table 8 shows that by simply cooling the mixture of 80 per cent. nitrogen and 20 per cent. helium to 77° K., we can separate it into 99·6 per cent. liquid nitrogen and 98 per cent. gaseous helium. For most technical purposes the purity of these products will be sufficient. By lowering the temperature still further, a yet higher degree of purity might be obtained. It is interesting to observe that the amount of helium dissolved in liquid nitrogen at first increases as the temperature is lowered and passes through a maximum at about 101° K.

Now take atmospheric air, which may here be considered as consisting

of 79 per cent. N_2 and 21 per cent. O_2, the other components being neglected. Suppose the air to be cooled at a constant pressure of 1 atm., and follow the process of condensation on the (T, x) diagram of Fig. 30. The equilibrium concentrations are here given by the ends of the horizontal connodals on the dew- and boiling-curve. The results are listed in Table 9.

TABLE 9. *Simple Condensation of Atmospheric Air at* 1 *atm.*

T	x_{O_2}	z_{O_2}	ϵ
81·4	49	21	0
81·0	46	17	0·12
80·0	35	13	0·37
79·0	24	8	0·80
78·8	21	6·5	1·00

From Table 9 it is evident that simple condensation will never lead to anything like a complete separation of oxygen and nitrogen. As the temperature falls through the inhomogeneous region, the oxygen concentration decreases simultaneously in both phases. When the boiling-point is reached the last bubble of vapour to condense contains 93·5 per cent. N_2, but in the meantime so much nitrogen has condensed that the liquid phase now has the same composition as the original gas. Simple condensation of oxygen–nitrogen mixtures produces only small changes in the relative concentrations of the liquid and gaseous phases.

From what we have said concerning simple condensation we may easily infer that the evaporation of a liquid, like the condensation of a vapour, may or may not lead to the separation of the components, the result depending on the shape of the equilibrium curves. The direction in which the change of phase is carried out is of subsidiary importance.

In considering the change of composition occurring during the evaporation of a liquid mixture, we must, however, distinguish between two possible conditions under which the evaporation may take place. The process may be conducted in such a way that the vapour formed remains in contact with the liquid throughout. On the other hand, it is more usual in practice to withdraw the vapour from the liquid as it is formed. In the first case, which is known as *closed evaporation*, at every stage of the process the whole of the vapour is, at any rate approximately, in equilibrium with the remaining liquid. In the second case, known as *open evaporation*, only the small amount of vapour just formed is in equilibrium with the liquid residue; the rest of the vapour, which has been withdrawn, no longer interacts with the liquid at all.

Consider the case of closed evaporation first. Let m_0 be the initial amount of liquid, and x_0 the concentration of the more volatile component. After an amount M has evaporated, let m be the amount of liquid left over and x its composition. The concentration of the more volatile component in the vapour will then be z, and vapour and liquid will be in equilibrium. Since the amount of the more volatile component in both phases together remains the same throughout the process,

$$mx+Mz = (m+M)x_0.$$

Therefore $$M/m = (x_0-x)/(z-x_0).$$

To determine x and z, when m, M, and m_0 are known, consider Fig. 54, in which z is shown as a function of x. From a point on the diagonal the abscissa of which is x_0 draw a straight line sloping upwards from right to left at an angle $\alpha = \tan^{-1}M/m$ with the vertical. This line intersects the z-curve at the point (x, z).† In the special case of perfect solutions x and z can be computed analytically.

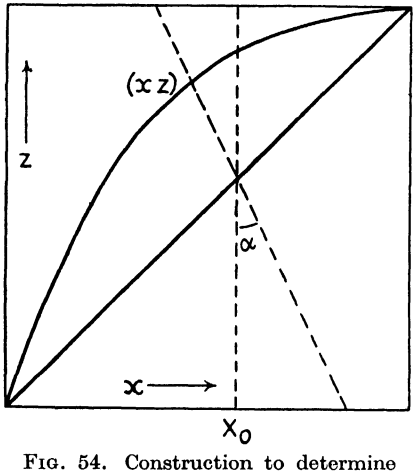


FIG. 54. Construction to determine change of composition during 'closed' evaporation

Now suppose the evaporation to be 'open'. When a small amount dM evaporates the composition of the liquid will change from x to $x+dx$, and the amount of liquid will change by $dm = -dM$. With the same considerations as before we obtain

$$mx-(m+dm)(x+dx) = z\,dM = -z\,dm,$$

whence, neglecting the product $dmdx$,

$$dm/m = dx/(z-x),$$

or

$$\log(m/m_0) = \int_{x_0}^{x} dx/(z-x).$$

This equation cannot, in general, be integrated except for a perfect solution with constant ϵ. It can, however, be integrated graphically in small steps as follows. Let a small amount ΔM evaporate. The amount of liquid will change from m_1 to $m_2 = m_1-\Delta M$ and its com-

† See Hausen, 'Materialtrennung durch Destillation und Rektifikation', *Der Chemie-Ingenieur*, I, part 3, ch. xv, § 13, p. 100 (Leipzig, 1933).

position from x_1 to x_2. The composition of the vapour will lie between z_1 and z_2, z_1 being in equilibrium with x_1, and z_2 with x_2. If ΔM is sufficiently small we can put $z = \frac{1}{2}(z_1+z_2)$. We then obtain

$$\Delta M\,\tfrac{1}{2}(z_1+z_2)+m_2x_2 = (m_2+\Delta M)x_1;$$

whence

$$x_1-x_2 = \frac{\Delta M}{2m_2}[z_2-(2x_1-z_1)].$$

In Fig. 55, in addition to z, the curve $2x-z$ has been drawn as a

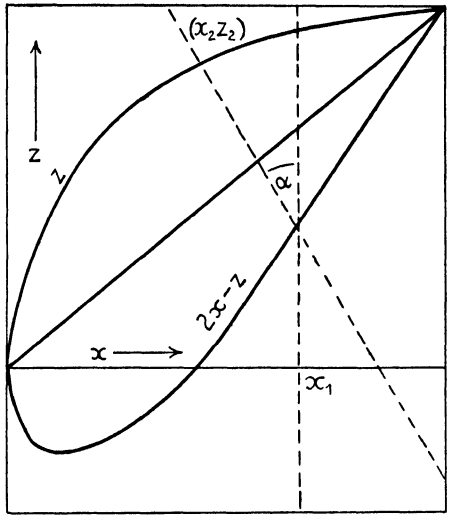


FIG. 55. Construction to determine change of composition during 'open' evaporation

function of x. This curve is easily obtained, as it is everywhere the same distance below the diagonal as z is above it. If we now draw a straight line through a point on the curve $2x-z$ with abscissa x_1, at an angle $\alpha = \tan^{-1}(\Delta M/2m_2)$, it will intersect the curve z at the point (x_2, z_2).

Figs. 56 and 57 show the course of closed and open evaporation of a perfect binary mixture with $\epsilon = 4$ (see equation (37), Ch. II) with an initial concentration of 80 per cent. of the more volatile component. The behaviour is similar to that of air. It will be seen that open evaporation enables the less volatile component to be obtained in a pure state, but with an infinitely small yield.

The design of condensers for use at low temperatures is largely determined by considerations of power economy. 'Cold' is much more expensive than heat, and the lower the temperature the dearer the cold.

Whereas at higher temperatures there is a marked tendency to increase the temperature differences between the two sides of a condenser and so economize in surface, at low temperatures it is generally more

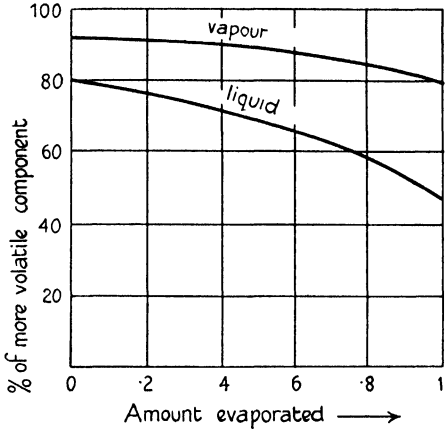


FIG. 56. Closed evaporation of a perfect mixture containing 80 per cent. of more volatile component. $\epsilon = 4$

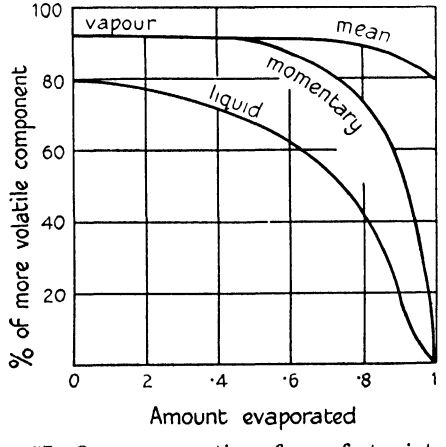


FIG. 57. Open evaporation of a perfect mixture containing 80 per cent. of more volatile component. $\epsilon = 4$

economical to keep the temperature differences small and to put up with large condenser surfaces. In the oil and chemical industries it is quite usual to employ cooling water at 15° C. to condense a vapour at 50 or 60° C. giving a temperature difference of 35–45° C. On the other hand, the temperatures on the two sides of a nitrogen condenser as

used in air-separating plants are never more than 3° and frequently less than 1° apart.

Similar considerations of power economy govern the use of latent and sensible heat in low-temperature condensers. Condensation of a pure substance takes place at a single temperature, but if the latent heat of condensation is to be taken up as sensible heat of a liquid or gas, the latter has to be heated through a finite temperature interval. As the refrigerant must leave the condenser at a temperature below that at which the vapour is condensing, it must enter at a still lower temperature which will depend on the rate of flow and on the specific heat. The circulation of very large quantities of cold liquids is not generally economical and the specific heats of the gases returning through separating plants are generally very low. The use of sensible heat for the cooling of low-temperature condensers would therefore result in very large temperature differences at the cold end between the condensing vapour and the refrigerant. Thus a great deal of cold would have to be supplied at temperatures far lower than that at which the actual duty is performed, and this would require the expenditure of much more work than is theoretically necessary.

As a consequence, the condensation of pure or almost pure substances or of a mixture with a narrow boiling range is almost always carried out in a 'condenser-evaporator', in which the latent heat of the condensing vapour is used to evaporate a liquid refrigerant.

The condenser-evaporators used in gas separation are generally of the vertical shell-and-tube type, a large number of straight narrow tubes being closely spaced between tube-plates in a cylindrical shell. Mild steel can be used down to temperatures of about −50° C., but below these temperatures it becomes too brittle and is generally replaced by copper. The plates, shells, and covers are sometimes made of bronze. The tubes are expanded into the plates and soft-soldered and the covers are bolted to the plates. According to the pressure in the shells, these can be of thin sheet or fabricated metal. In some cases castings are used.

Generally the condensing vapours pass through the tubes of the condenser and the refrigerant evaporates in the shell. A photograph of a typical condenser-evaporator is shown in Fig. 111, p. 168.

Similar units are frequently used to secure partial condensation of a mixture and phase separation. Fig. 58 shows an example in which the liquid formed in the tubes of a condenser at an elevated pressure itself serves as the refrigerant at a lower pressure after being fed through a

reducing valve to the shell, while the uncondensed vapour, still at the higher pressure, escapes through the cover.

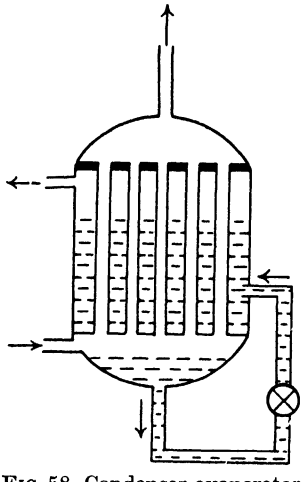


FIG. 58. Condenser-evaporator

This type of condenser-evaporator, fed with a foreign refrigerant, is found in the condensation of methane from coke-oven gas in the production of hydrogen–nitrogen mixtures for ammonia synthesis. In this case the refrigerant is liquid nitrogen supplied from a special cycle. The process will be discussed in detail in Chapter X. In air separation (see Chapter VI) a similar arrangement is used to condense nitrogen under pressure with the help of liquid oxygen boiling at atmospheric pressure. Here the condensing vapour and the refrigerant are part of the same air which is being separated.

2. Dephlegmation

Consider the condenser-evaporator depicted in Fig. 58, and suppose that the vapour condensing in the tubes and the liquid boiling between the tubes are one and the same binary mixture. As we have seen, a mixture condenses in a finite temperature interval and the composition of the liquid formed varies as the condensation proceeds. A temperature head will therefore tend to be set up between the top and bottom of the apparatus inside the tubes in which the vapour is condensing. The temperature at the bottom of the tubes will correspond roughly to that of the commencement of condensation, and the temperature at the top will be lower. Simultaneously, there should be a difference in composition in respect to each phase between the top and the bottom.

Consider a certain section of a condenser, through the tubes of which a mixture of oxygen and nitrogen is passing at 5 atm. Suppose the initial composition of the mixture on entering the condenser from below was 50 per cent. N_2 and 50 per cent. O_2. If the temperature of the liquid between the tubes is sufficiently low, a certain amount of the mixture will have condensed by the time it has reached the section. If, say, one-third has condensed, we may infer from the equilibrium diagram of Fig. 30 that the gaseous phase will contain about 43 per cent. O_2 and the liquid some 67 per cent. O_2. But the liquid, owing to its greater specific gravity, will for the most part drip downwards along

the walls of the tubes and never reach the higher sections of the condenser. Now, if the walls of the tube are cold enough, the vapour, as it rises above the section, will continue to condense. It will, in fact, behave just as the original vapour of 50 per cent. O_2 behaved, only now it will contain only 43 per cent. O_2. Suppose that when it has reached a higher section another third has condensed. From the (T, x) diagram we may conclude that the gas will now contain 35 per cent. O_2. Apparently, if the condenser is long enough and the liquid between the tubes cold enough, this process can be carried on indefinitely.

The numerical data that we have just given are obviously rough and our arguments at the best approximate. All they really show is that the vapour in the upper part of the condenser will contain less oxygen than that condensed at the bottom. Actually we shall have a current of comparatively warm gas moving upwards and a stream of cold liquid trickling downwards along the walls of the tubes. The vapour will interact not with the walls directly but with the layer of liquid trickling down them. This liquid will contain more oxygen than the gas with which it interacts but less oxygen than a liquid should contain that is in equilibrium with the vapour interacting with it. Part of the gas will condense, the liquid formed containing more oxygen than the vapour itself, and part of the liquid will evaporate, the vapour formed containing less oxygen than the liquid. As a result, the liquid trickling down the tubes will gradually become enriched with oxygen as it moves downwards, and the vapour will simultaneously become enriched with nitrogen on its way up the condenser. The liquid escaping from the bottom of the condenser cannot contain more oxygen than is in equilibrium with the gaseous mixture entering the tubes, but if the condenser is long enough and the refrigerating liquid cold enough, the vapour emerging at the top of the condenser may come to be almost pure nitrogen.

This procedure, which was first applied in low-temperature gas separation by Claude, is called *dephlegmation*, and a condenser so constructed as to enhance this effect as much as possible is termed a *dephlegmator*. The liquid formed in a dephlegmator and emitted downwards through the tubes is known as *reflux*.

Now suppose that in a dephlegmator, of the type shown in Fig. 59*a*, the mixture entering at A is atmospheric air, precooled to the temperature at which condensation commences at the working pressure. We shall leave this pressure undetermined for the time being. We have seen that the vapour emerging at E can be almost pure nitrogen, and

we shall suppose for the moment that the nitrogen is really pure. The liquid collecting at B may at the best have a composition corresponding to that of a liquid in equilibrium with atmospheric air at the working pressure. Actually it will contain a little more nitrogen. Suppose that we maintain 55 per cent. nitrogen at this point, a figure always obtainable. Within the tubes a temperature head will be set up, corresponding

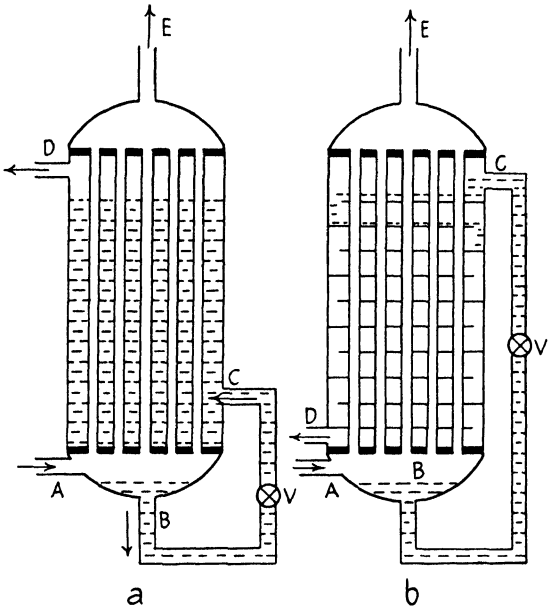


FIG. 59. Dephlegmators: *a*, normal type; *b*, with trays

to the difference in the boiling-points of pure nitrogen and the liquid mixture formed at B.

Suppose that this liquid is expanded in the valve V to atmospheric pressure and delivered between the tubes of the condenser. Part will evaporate during the expansion, the rest as a result of condensation inside the tubes. Finally, all the liquid formed at B will emerge at D as a saturated vapour. The vapour leaving at D will, therefore, have the same composition as the liquid at B, i.e. 55 per cent. nitrogen. But in the stationary state the liquid boiling between the tubes will contain more oxygen than the vapour emitted at D. Its composition will, in fact, be that of a liquid in equilibrium with this vapour, namely, 22 per cent. nitrogen. And since the vapour from this boiling liquid is ejected at D immediately it leaves the surface of the liquid, the composition of the liquid will be practically the same throughout. Its temperature will, therefore, also be the same throughout. This temperature will be

85·3° K., the boiling-point, at atmospheric pressure, of a liquid containing 22 per cent. nitrogen. Outside the tubes there will be no appreciable temperature head between the top and bottom of the dephlegmator.

In order that heat may be transferred from the condensing vapour inside the tubes to the liquid boiling outside, the latter must be colder than the former. We shall assume that the surface of heat transfer is such as to require a temperature head of 4° C. between the inside and outside of the tubes, in order that the necessary quantity of heat may be transferred. Since the temperature inside the tubes varies with the height, this means that the temperature of the liquid outside must be 4° lower than that of the vapour condensing at the top, i.e. at the coldest point inside the tubes. But we have assumed that this vapour is pure nitrogen. So the temperature of the nitrogen must be 85·3+4 = 89·3° K. The vapour pressure of nitrogen boiling at 89·3° K. is 3·3 atm. abs. This is therefore the pressure that must be maintained inside the tubes. To keep the process going, all the air must be compressed to 3·3 atm. This pressure determines the power consumption necessary to keep the plant working. It is therefore of importance to have the pressure as low as possible.

Now the temperature in the tubes at the bottom of the dephlegmator is the boiling-point, at 3·3 atm., of a mixture containing 55 per cent. nitrogen. This is 93·5° K. So the temperature head between condensing vapour and boiling liquid at the bottom of the apparatus is 93·5−85·3 = 8·2° C. This temperature head is unnecessarily high. It gives us more than we require and we may conceivably think that a more suitable construction of the dephlegmator might reduce the pressure needed to keep it working.

The fact that this type of dephlegmator gives rise to a temperature head between top and bottom inside the tubes, but not to a corresponding temperature head outside, is an important drawback, which we can best gauge by studying the effect of its elimination. Fig. 59*b* shows a dephlegmator of another type. The space between the tubes contains a series of horizontal trays, each with an aperture at the side. The liquid mixture that collects at *B* is admitted, after expansion, to the topmost tray at *C*. It trickles down from one tray to the next, evaporating all the time. Finally, when all has evaporated, the vapour emerges at *D* at the bottom of the apparatus.

In this case the vapour remains in contact with the liquid throughout the extent of the dephlegmator. The result of this is that the

concentration of liquid and vapour varies from tray to tray. In our example the liquid at the top contains 55 per cent. nitrogen, and only the last drops of liquid, evaporating from the lowest tray, contain 22 per cent. nitrogen. For the same reason the temperature in the space between the tubes also varies with the height, from the boiling-point of a liquid with 55 per cent. nitrogen to that of a liquid containing 22 per cent. nitrogen, that is to say, from 81° to 85·3° K.

The temperature of the nitrogen leaving the top of the tubes must now be $81+4 = 85°$ K., which corresponds to a pressure of 2·2 atm. abs., and that of the liquid at B should be $85·3+4 = 89·3°$ K., which requires 2·3 atm.

Thus, with the help of these trays, the same effect can be achieved with 2·3 atm. which formerly required 3·3 atm. Under certain circumstances the power economy thus gained is of paramount importance.

Dephlegmators of various types play an important part in a number of gas-separating plants. They were first developed in air separation in a process for the production of what is known commercially as 'rich air'. This is a mixture containing from 40 to 60 per cent. oxygen, which is employed to raise the efficiency of combustion in furnaces. To obtain a mixture of this composition, for use in blast-furnaces, was one of Linde's original ideas, when he first created low-temperature gas separation; but only in recent years has it become possible to produce rich air at sufficiently low costs to warrant its application in metallurgy.

Dephlegmation is also at the basis of most processes for obtaining pure helium from natural gases (see Chapter XI).

3. Rectification

Dephlegmation is a particular and not very efficient application of a much more general principle. A current of gas and a stream of liquid, which are *not* in equilibrium with one another, are conducted in opposite directions, the surface along which they interact being made as great as possible. Then the vapour will become enriched with the component with the lower boiling-point and the liquid will become richer in the component that boils at a higher temperature. This principle, which is known as *rectification*, is by far the most powerful instrument in the separation of gases.

To grasp the significance of rectification let us turn again to the (T, x) diagram of oxygen–nitrogen mixtures, as a typical example of a binary solution the boiling-points of whose components lie fairly close together (see Fig. 60). This diagram, which holds for constant pressure,

shows clearly that a vapour and a liquid in equilibrium have always different compositions and, conversely, that a vapour and a liquid having the same composition cannot be in equilibrium with one another. Suppose a liquid and a gaseous mixture, both having the same composition and both being in a state of saturation, to be brought into contact. The states of vapour and liquid may be described by the points A and B in Fig. 60. It is important to observe that the two phases will be at different temperatures, the vapour being warmer than the liquid. The two phases will mix and eventually reach a state of equilibrium. This state will be characterized by a composition equal to that of A and B and a temperature between A and B, and may be depicted by point C. The exact position of C between A and B will, of course, be determined by the relative quantities of the mixtures A and B. C at all events lies in the inhomogeneous region, which means that the resulting vapour and the resulting liquid will lie at the ends of the connodal through C, i.e. at D and E, and will thus have *different* compositions. So if a liquid and a vapour having the same composition are brought into contact, the compositions of liquid and gaseous phase will *move apart*; the liquid will finally contain more and the vapour less of the component with the higher boiling-point. This is the basic phenomenon underlying rectification.

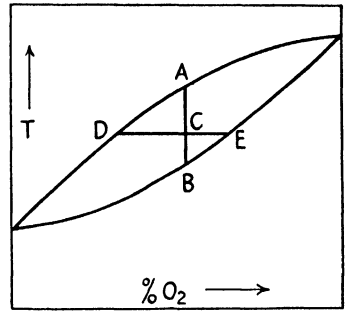


FIG. 60. Illustration of rectifying process on (T, x) diagram

In order to make the most of this principle, it is essential that the liquid and the vapour be brought into such intimate contact that equilibrium is as nearly as possible attained, as otherwise the ultimate compositions of the two phases will differ less than points E and D in the figure. It is therefore important to bring about a large surface of interaction between the liquid and the vapour. In practice this is achieved best in the so-called *rectifying column*, in which the vapour is passed through a number of liquid layers.

There are two well-known types of rectifying columns: packed columns and plate columns. The former are simply cylindrical towers packed with a suitable material offering a large surface per unit volume. Raschig rings are frequently used, but more recently a number of other packing materials have been suggested which claim particular advantages.†

† J. A. Weedman and B. F. Dodge, *Ind. Eng. Chem.* **39**, 732 (1947); H. O. McMahon, ibid. **39**, 712 (1947).

Most of the columns used in gas separation are fitted with plates which are so arranged to bring about the best possible contact between liquid and vapour. One type of plate, developed principally by the German Linde Co., for use in air separation, is a thin metal disk with a large number of perforations. In the Linde plates the perforations are 0·8 mm. in diameter with a 3 mm.-spacing. The pressure of the rising vapour is sufficient to prevent the liquid from escaping downwards through the perforations, which serve to pass the gas upwards in the form of very small bubbles. The liquid leaves the plates over one or more low weirs and descends through a vertical tube or 'downspout' which forms a seal with the liquid on the plate below. Generally the weirs are arranged on alternate sides of successive plates, so that the liquid flows across the plates in alternate directions. In more up-to-date columns the plates are annular with a cylindrical former in the middle of the column, and the liquid flows around the plates in a circle. The weirs are at right angles to the direction of flow and so arranged that this direction is the same on each plate. The reasons for this arrangement will be discussed in Chapter VIII.

The bubble-cap plate is an alternative form which is used extensively in the oil and chemical industries and has been introduced in low-temperature gas separation fairly recently. Instead of the very large number of small perforations the plate carries a smaller number of larger holes through which tubes are inserted which protrude above the plates. To these so-called 'up-spouts' are attached the bubble-caps in the form of inverted cups with a large number of serrations at the edge which may be rectangular or triangular in shape. The vapour rises through the upspouts, is turned downwards by the caps, and emerges on to the plate horizontally through the serrations. The weirs and down-spouts are similar in the two types, both of which have advantages and disadvantages.†

The perforated plates lead to more and smaller bubbles and hence to better contact between the two phases. They are also less liable to cause entrainment of liquid with the vapour. On the other hand they are very sensitive to changes of throughput. If the flow of vapour decreases, there is always a danger of the liquid drawing off the plate through the perforations, and when the rate of flow is too great, the bubbles coalesce too rapidly and a thick layer of foam leads to entrainment of liquid on to the plate above. Perforated plates are therefore most useful in cases of fairly constant load.

† N. M. Zhavoronkov and I. E. Furmer, *Kislorod*, No. 5, p. 9 (1947).

Bubble-caps are far less sensitive to throughput and variation in vapour flow can be taken up within wide limits without much loss of efficiency. In Chapter VIII the action of the rectifying plate will be studied in rather greater detail.

The spacing between successive plates varies greatly in different industries, depending on the gas velocities and the nature of the substances treated. In most oil fractionating towers where bubble caps are used, the spacing is between 12 and 18 in.; in air separating columns using perforated plates 4–5-in. spacing is used. The lower limit of the spacing is set by two considerations: accessibility and entrainment. In many cases of fractionation at high temperatures the mixtures contain solid impurities which require frequent cleaning of the plates and it is therefore customary to insert a man-hole in the column wall between every pair of plates. It is then convenient to have the plates some distance apart. In low-temperature columns the only solid impurities are those that are precipitated at the low temperatures. To clean the plates it is only necessary to warm up the column and the deposits melt away or sublime off. Mechanical cleaning is seldom required and the man-holes are superfluous. It is then possible to space the plates closer together.

Entrainment of liquid is mainly a function of the mass velocity of the vapour, and for a given throughput can be varied by altering the diameter of the column. It has been found that much of the entrained liquid falls back on to the plate if the distance to the next plate above is sufficiently great.† In high-temperature plant, especially where the throughput is very great and the reflux ratio high, it is economical to use high velocities and narrow columns with large spacing and consequent greater height. When working at low temperatures, tall and narrow columns are a disadvantage mainly because of the high cost of thermal insulation. In order to keep these costs low and also for a number of other reasons which need not concern us here, it is not advisable to erect these columns in the open. The tall narrow columns require not only lavish insulation but also high buildings to protect the insulation. It is thus more economical to shorten the columns and increase their diameter to enable the spacing to be reduced.

A photograph of a typical air separating column is shown in Fig. 114, p. 168.

The depth of liquid on the plates also varies greatly. A large depth

† M. Souders and G. G. Brown, *The Refiner*, **13**, No, 1, p. 32 (1934); G. E. Holbrook and E. M. Baker, *Ind. Eng. Chem.* **26**, 1063 (1934); *Trans. Am. Inst. Chem. Eng.* **30**, 520 (1934).

of liquid offers better contact between the phases as the bubbles remain in the liquid longer; on the other hand it increases entrainment, causing jets of liquid to be shot out of the surface. Thus for the same reasons as were mentioned above, low-temperature columns use shallower liquid than columns working at high temperatures; whereas $1\frac{1}{2}$ in. is customary in the oil industry, gas-separation plant generally keep to a $\frac{1}{2}$ in. depth of liquid on the plates.

A rectifying plate may be taken as an example of a separating surface of the kind described in the Introduction, and rectification in a plate column exemplifies gas separation in a finite number of steps across a corresponding number of surfaces. Of course, the surfaces themselves are formed by the interfaces of the bubbles of vapour. The actual metal plate is merely a framework which enables the surface to materialize.

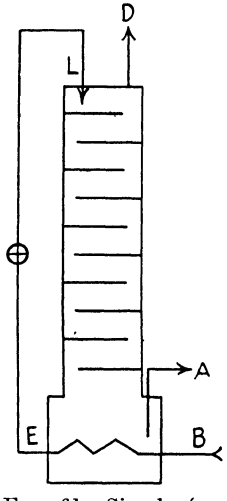


FIG. 61. Simple 'exhausting' column

A packed column is an example of a virtually infinite number of separating surfaces and separation occurring in an infinite number of stages. The main disadvantage of packed columns is their tendency to channel, i.e. for liquid to move outwards and to flow down the walls instead of through the packing. This tendency is the more marked the wider the column and hence packed columns are used mainly for small capacity plant. Channelling can be reduced by careful packing, and some packing materials have recently been suggested which claim to avoid this disadvantage.

Packed columns are in general cheaper than plate columns and the decision to employ one or another type is generally one of economics. In making the decision it is important to know the efficiency of each, and this is generally defined in terms of the height of a transfer unit. This is the depth of packing which is equivalent to one 'theoretical plate'. In Chapter VIII the concept of the theoretical plate will be further developed.

In the type of column shown in Fig. 61, the liquid mixture is introduced at L from above, after being condensed in the re-boiler between B and E and expanded. It falls from plate to plate, and is partially or wholly evaporated at the bottom of the column. In the stationary state, a continuous flow of liquid is maintained in a downward direction, and a continuous current of vapour rises upwards through the liquid. The separated products are finally emitted at A and D.

The 'exhausting' column sketched in Fig. 61 has a similar drawback to a dephlegmator: it allows only one component of the binary mixture to be obtained in a state of purity. Referring again to the example of atmospheric air, we see that, while a dephlegmator can produce pure nitrogen, but not pure oxygen, a column of this type can give pure oxygen, but not pure nitrogen. For the vapour leaving the column at D cannot contain more nitrogen than is in equilibrium with the liquid air entering at L. A vapour in equilibrium with atmospheric air at 1 atm. pressure contains 93 per cent. of nitrogen. Purer nitrogen cannot be obtained with this kind of column. To obviate this difficulty the column may be prolonged above the inlet at L and fitted with a condenser at the top, as shown in Fig. 62. The condenser maintains a reflux in the upper part of the column and enables pure nitrogen to be emitted at D. However, the condenser requires a source of refrigeration at the top of the column, which is not always easily obtainable. In the figure we have merely hinted at this source by intimating that an amount of heat Q must be removed from the column at this point. We shall see in Chapter VI how this is achieved in practice.

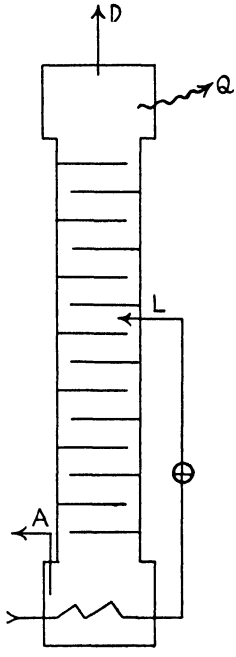


FIG. 62. Rectifying column extended to condenser above inlet

4. Heat-exchangers

It is customary to use the term heat-exchanger to denote a unit in which mainly sensible heat is transferred, whereas condensers and evaporators transfer principally latent heat through a change of phase of at least one of the streams. In gas-separation plants heat-exchangers are used occasionally for the sub-cooling and re-heating of liquids, but their most important function is to cool the gases to be separated down to their dew-points by means of cold gaseous products, which are warmed up in this way to closely below ambient temperature. 'Gas–Gas Exchangers' are therefore an important feature in gas separating plant, and their efficient design offers a number of difficulties.

The heat transfer from gas to gas through metal walls is in general bad, and reasonable heat-transfer coefficients can only be obtained with high velocities. On the other hand high velocities lead to a high resistance and a consequent large pressure drop in the exchanger which can

seldom be afforded. Moreover, every transfer of heat from a higher to a lower temperature is irreversible and leads, as will be shown in the next chapter, to additional power consumption which is the more considerable the lower the temperature at which the transfer takes place. It is therefore necessary to keep the temperatures of the two gas streams as close as possible, and so the combined effect of low transfer coefficients and small temperature difference necessitates very large surfaces and frequently leads to very inconvenient shapes. Several types of exchanger have therefore been developed for use in gas separating plants, and some of them differ considerably from those employed in other industries.

For the theory and practice of heat transfer by convection, the reader is referred to the appropriate text-books,† but a few points may be mentioned here to illustrate the problems involved and to account for the particular solutions that have been found suitable for gas-to-gas exchangers in separating plant.

The heat Q (kcal./hr.) transferred in unit time across a surface A (m.^{2}) is generally written in the form

$$Q = UA\,\Delta T_m, \tag{1}$$

where U is the heat-transfer coefficient in kcal./hr. m.^{2} °C. and ΔT_m is the logarithmic mean temperature difference, which is formed from the temperature differences ΔT_1 and ΔT_2 between the two streams at the ends of the exchanger by the relation

$$\Delta T_m = \frac{\Delta T_1 - \Delta T_2}{\ln(\Delta T_1/\Delta T_2)}. \tag{2}$$

The reciprocal heat transfer coefficient $1/U$ is considered as a resistance and is made up of three terms, two of which involve the film coefficients h_1 and h_2 from gas to wall and from the wall to the other gas and the third contains the thickness of the wall d and its thermal conductivity k:

$$\frac{1}{U} = \frac{1}{h_1} + \frac{d}{k} + \frac{1}{h_2}. \tag{3}$$

In most gas-to-gas exchangers, in which the gases are conducted through copper tubes, k is so large, and h_1 and h_2 so small, that the second term can be neglected in comparison with the other two and we can write

$$U = \frac{1}{(1/h_1)+(1/h_2)}. \tag{4}$$

For the case of turbulent flow in tubes, which is usual in gas heat

† e.g. W. H. McAdams, *Heat Transmission*, 2nd ed. (McGraw-Hill, 1942).

exchangers, the dimensionless expression $Nu = hD/k$, which is known as Nusselt's number, is proportional to the 0·8th power of the Reynolds number $Re = DG/\mu$ which must be well above 2,200 to ensure turbulence.

h is the film coefficient,
k the thermal conductivity of the gas,
D the internal diameter of the tubes,
μ the viscosity of the gas, and
$G = v\rho$ the mass velocity, considered as weight per unit time per unit cross-section,
v is the linear velocity, and
ρ the density of the gas.

The experimentally determined proportionality constant is generally taken as 0·016, so that

$$\frac{hD}{k} = 0{\cdot}016\left(\frac{DG}{\mu}\right)^{0{\cdot}8}. \tag{5}$$

For flow outside and parallel to tubes, the same formula holds, but the D on the left-hand side is now the external diameter, and the D that enters into the Reynolds number on the right is the so-called hydraulic diameter, which is four times the free cross-section divided by the perimeter.

In low-temperature gas-separating plants the gas-to-gas heat exchangers of the conventional shell-and-tube types are almost always inconveniently long, especially if the temperature interval between the ends is large. Without a radical change in the design of the exchangers it is not generally possible to reduce the length to reasonable limits. This can be shown fairly simply as follows: Let

R be the throughput of the exchanger in weight per unit time,
C the specific heat of the gas, assumed to be constant,
ΔT the temperature difference between the warm and cold ends,
ΔT_m the log mean temperature difference across the exchanger,
Q the amount of heat to be transferred in unit time,
N the number of tubes,

and let U, h, A, and D have the same meaning as above. Then

$$Q = RC\Delta T = UA\Delta T_m, \tag{6}$$

and since $A = N\pi DL$, where L is the length of the tubes,

$$L = \frac{C}{\pi\Delta T_m} \times \frac{R\Delta T}{NUD}. \tag{7}$$

Now assume for simplicity that the film coefficient h is the same inside and outside the tubes. The $U = \frac{1}{2}h$ and

$$L = \frac{C}{\pi \Delta T_m} \times \frac{2R\Delta T}{NhD}. \tag{8}$$

Inserting (5) in this equation, and noting that

$$G = \frac{4R}{N\pi D^2}, \tag{9}$$

(8) becomes

$$L = \left\{\frac{C}{0{\cdot}008\pi k} \times \left(\frac{\pi\mu}{4}\right)^{0{\cdot}8}\right\} \frac{\Delta T}{\Delta T_m} \left(\frac{R}{N}\right)^{0{\cdot}2} D^{0{\cdot}8}. \tag{10}$$

For our present purpose the expression in brackets may be considered as a constant B so that

$$L = B \frac{\Delta T}{\Delta T_m} \left(\frac{R}{N}\right)^{0{\cdot}2} D^{0{\cdot}8}. \tag{11}$$

Now if a heat-exchanger is to cool a certain amount of gas in unit time through a specified temperature interval with an agreed log-mean temperature difference, ΔT, ΔT_m, and R are given, and the only variables are N and D. But a decrease in the diameter of the tubes necessitates an increase in their number. The gas velocity will be chosen as high as is compatible with the pressure drop allowed, and the total cross section $N\pi D^2/4$ will therefore be virtually a constant. Hence N will vary inversely as D^2 and L will be proportional to $D^{1{\cdot}2}$.

Equation (11) shows that L is also directly proportional to the temperature interval through which the gas is to be cooled.

Now if we consider an exchanger in which air is cooled from room temperature to close to its dew-point, ΔT is about 200° C. and B is found, by inserting the appropriate values of C, k, and μ, to be 126. Putting $\Delta T_m = 6°$ C., which is commonly used in practice, and choosing a suitable gas velocity, we obtain

$$L \sim 4{,}200 D^{1{\cdot}2}, \tag{12}$$

where L and D are both in centimetres. Thus for tubes of 1 cm. internal diameter ($\frac{3}{8}$ in.), which are frequently used in gas-separating plant, $L = 42$ m. $= 138$ ft.; and for 5-mm. tubes, which are about the narrowest used in practice, $L = 60$ ft.

In the case of gases other than air, the position is no better, for although ΔT is generally smaller in view of the higher boiling-points of most of these gases, the specific heat is mostly higher and the thermal conductivity lower. Thus to cool ethylene by $\Delta T = 100°$ C., the lengths required for 1-cm. and 0·5-cm. tubes are 160 ft. and 70 ft. respectively.

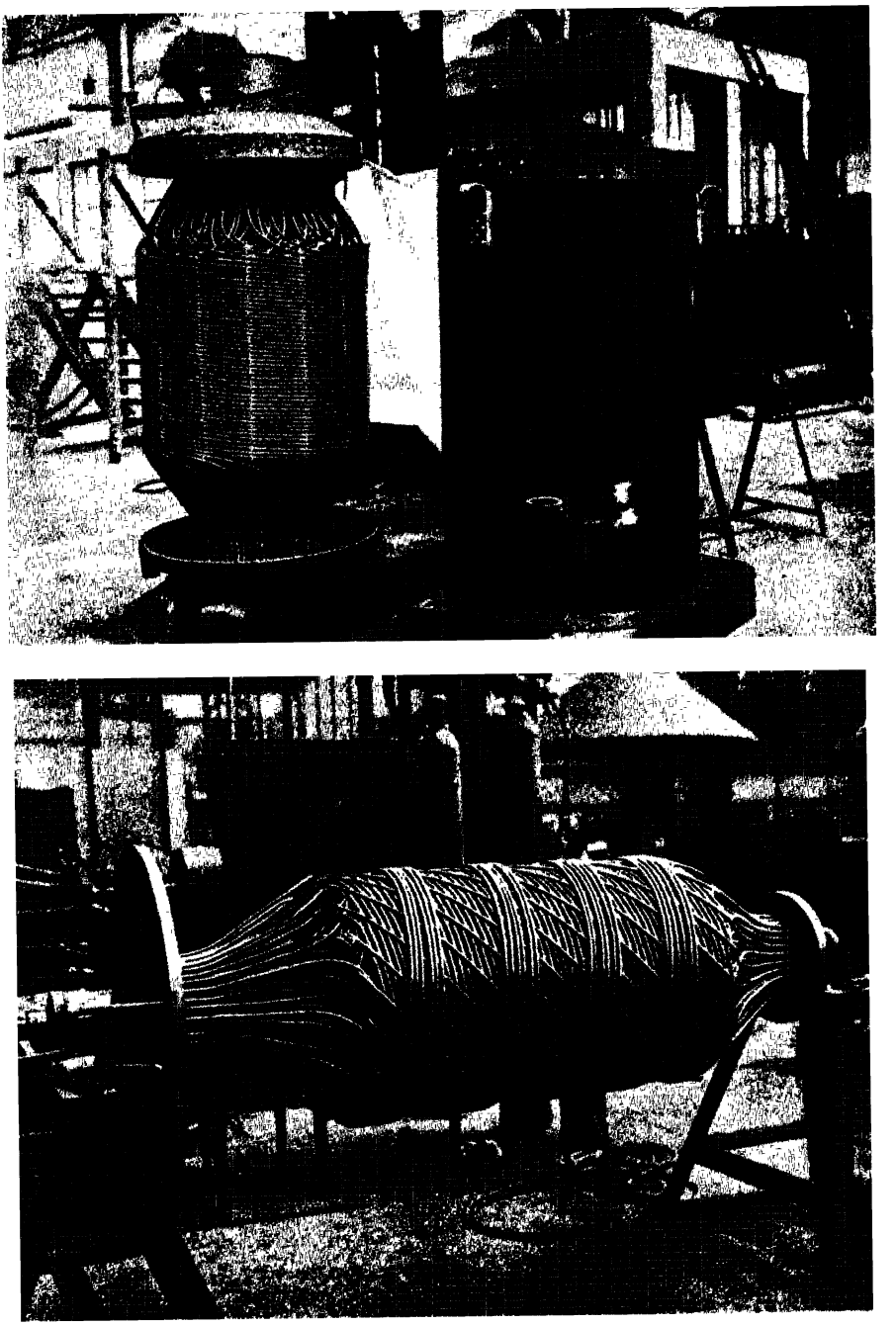


FIG. 63. Cross-countercurrent heat exchangers of the Société Anonyme Air Liquide
(Reproduced with permission of the Iron and Coal Trades Review)

Two different types of exchanger have been evolved to overcome this difficulty, of which one is generally known as 'tube-in-tube' and the other as the 'cross-countercurrent' heat-exchanger. The former type consists of a helical coil of wide tubing which forms the shell and contains a relatively small number of narrow tubes within it. In the cross-countercurrent exchanger a number of narrow tubes are wound helically around a core in several radial layers and the whole is contained in a shell with two circular plates through which the tubes pass to a collector or manifold. In this unit one stream travels helically through the tubes and the other passes across them in countercurrent. The result is a combination of cross- and counter-flow from which the exchanger bears its name.

Coiled tube-in-tube exchangers were used frequently in the past in air separation plants where the air passing through the tubes was at a very high pressure and where, therefore, large quantities of air could be passed through a relatively small number of tubes without a prohibitive pressure drop. At lower pressures, or in very large plant, the number of tubes becomes excessive for this design as the bundle becomes too thick and the pressure drop outside the tubes tends to be high. For these duties cross-countercurrent exchangers offer important advantages. They are designed in such a way that all tubes are of the same length so as to make sure that the same amount of gas passes through each. Fairly high heat-transfer coefficients of 100 kcal./m.^{2} hr. °C. and over can be obtained in compact units without high pressure drops, and it is easy to include several separate streams passing in parallel through groups of tubes.

The wound length of a cross-countercurrent heat-exchanger is $1/2\pi$ times the length of the individual tubes. The air cooler described above, which would be 138 or 60 ft. long as a straight-tube exchanger with tubes of 10 and 5 mm. diameter respectively, would be 22 ft. or 10 ft. long if designed on the cross-countercurrent principle. The increased film coefficients due to the cross-countercurrent flow, which have not been taken into account, would reduce the required length still further. Typical cross-countercurrent exchangers are shown in Fig. 63.

5. Regenerators

The larger a gas-separating plant, the greater the amount of heat that has to be transferred from the incoming gas mixture to the outgoing products and the bulkier and the more expensive the heat-exchangers become. It was, therefore, an important advance when Fränkl in 1928 suggested using regenerators or cold accumulators for low-temperature

gas-separation. These units are now used generally in the oxygen industry for large capacity plant, and they have recently been applied successfully in the separation of coke-oven gas.

The regenerator is a tower packed with a material of a relatively high heat capacity, and two such towers are needed to replace one heat-exchanger. If heat is to be exchanged between a warm and a cold gas,

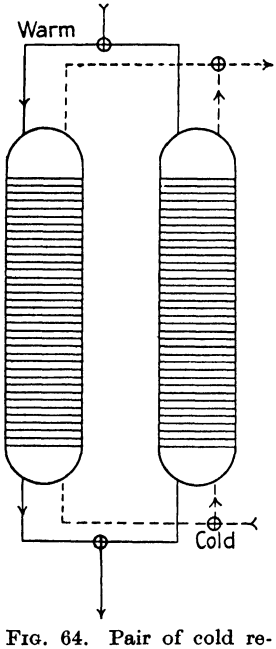


FIG. 64. Pair of cold regenerators with valves for reversing gas current

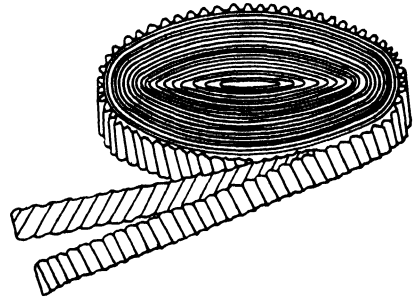


FIG. 65. Typical regenerator packing

the two streams are passed through the two regenerators in opposite directions for a brief space of time and the currents are then reversed. In this way, each regenerator is traversed alternately by each gas stream, the warm stream passing, say, from top to bottom and the cold stream from bottom to top. In one period the cold stream cools the packing material, and in the other this cold is transferred to the warm gas. The arrangement is shown in Fig. 64.

The regenerators are usually packed with flat disks, 35–50 mm. wide, wound from thin corrugated aluminium ribbon 0·2–0·4 mm. thick. The corrugations are 1·5–3 mm. deep and slant in opposite directions on alternate strips as shown in Fig. 65. An alternative design proposed by Kapitza uses alternately smooth ribbons and ribbons with small protuberances punched at regular intervals.

If a cold and a warm current of gas are alternately passed through a pair of regenerators for periods of a few minutes, a stationary state is finally reached after several hours in which the temperature distribution along each regenerator is practically linear, except in a small portion near the end (see Fig. 66). Between the end of the warm and the end of the cold period, the straight line representing the temperature as a function of the distance from one end of the regenerator is merely shifted slightly parallel

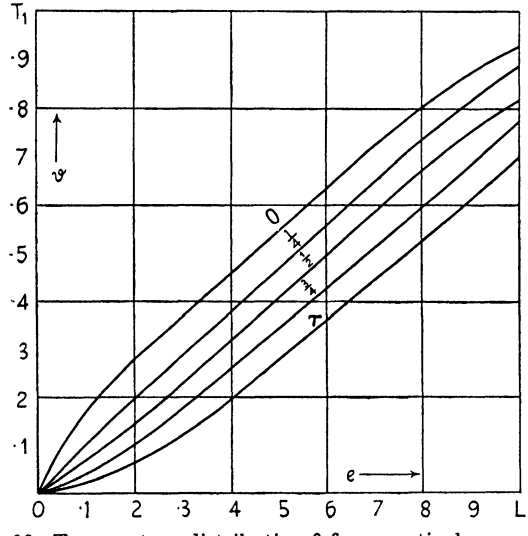


FIG. 66. Temperature distribution ϑ for a particular case of a gas passing through a regenerator, after the steady state has been reached, in four phases of the cold period τ, as a function of the distance l from the cold end

L = length of the regenerator;

T_1 = temperature of warm gas minus temperature of cold gas at entry. Cold and warm periods are assumed to be of equal length. ϑ is the temperature of the gas, not that of the filling material.

to itself. This is shown in the figure for the case of air being cooled from room temperature to its boiling-point by a stream of cold nitrogen.

Alternating regenerators have a number of very important advantages as compared with normal heat exchangers.

1. They are relatively cheap and easy to manufacture.
2. They enable a very large surface to be concentrated into a small volume. Most regenerators have a surface of 1,000 to 2,000 sq. ft. per cu. ft.
3. Suitably designed regenerators have a low hydraulic resistance and thus allow the passage of large quantities of gas with a very small loss in pressure.

4. Regenerators allow some impurities to be deposited by the warm gas in one period and to be re-evaporated by the cold gas in the other period, thus eliminating the need for chemical purification in certain cases.

This applies in particular to the removal of moisture and carbon dioxide from the air in large plants producing oxygen of not very high purity. Ice and solid CO_2 are precipitated on the regenerator surface from the air in the warm period and sublimed by the dry, cold products in the cold period.

On the other hand, regenerators have certain inherent disadvantages, and they cannot be made to replace heat exchangers under all circumstances.

It is, for instance, not generally possible to obtain very pure products with plants using regenerators. At the beginning of the cold period the regenerator contains the unseparated gaseous mixture, and the cold product has to purge this out, thus itself becoming contaminated. The extent of this contamination depends on the lengths of the cold and warm period; the longer this period, the smaller the impurities of the products. It has been found economical to produce in regenerator plant oxygen of a purity up to 98 per cent. It is, of course, possible to discard a certain amount of product at the beginning of each cold period, and thus to obtain purer products, and this has been done in some German oxygen plants; but this procedure lowers the yield and so increases the power consumption per unit of product.

A further condition for the satisfactory working of regenerators is that the amount of gas in each stream shall be approximately the same, and that the temperature differences between the two streams shall be small. Moreover, since the same passage is used alternatively by each stream, it is not practicable for one stream to be at a very high pressure when the other is close to one atmosphere.

In short, regenerators are eminently suitable for the exchange of heat between two large and similar gas streams, conditions which occur very frequently in practice. They are not suitable when the streams are very dissimilar, either as regards pressure, temperature, or rate of flow.

The greatest practical advantage of regenerators is that they avoid chemical drying and removal of CO_2 by absorption. Snow and solid CO_2 are the main dangers of low-temperature gas-separation as they block up the pipes and lower the heat transfer coefficient by forming films on all metal surfaces. The conditions in which regenerators are self-purging in respect of ice and CO_2 are narrowly defined, and if they are not strictly observed, the regenerators will block up rapidly and be useless.

To ensure complete purging, the return cold gas must be able to take up more CO_2 and water vapour from every cross-section of regenerator surface than the warm gas mixture was able to deposit in the previous period. The fact that the return gas is at a lower pressure than the incoming gas makes it more capable of subliming deposits, but the fact that it is at a lower temperature makes it less able to do so.

Consider, as an example, the removal of CO_2 from air in a regenerator passing warm air in one period and cold nitrogen in the other. Suppose for the moment that both gas streams are saturated with CO_2 at a certain cross-section of a regenerator. Then the regenerator will purge if the amount G of CO_2 deposited by the warm air is less than the amount G' which can be sublimed by the cold nitrogen. This can be expressed by the relation

$$M = G - G' = \gamma\left[\frac{v}{p}\frac{d\pi_c}{dT} - \frac{v'}{p'}\frac{d\pi'_c}{dT}\right] < 0, \tag{13}$$

where γ is the specific gravity of CO_2,

π_c its vapour pressure at the temperature T of the air,

π'_c its vapour pressure at the lower temperature T' of the nitrogen,

p the total pressure of the air,

p' the total pressure of the nitrogen,

v the flow of air (say in N m.^{3}/hr.), and

v' the flow of nitrogen.

The vapour pressure equation for CO_2 can be written

$$\log \pi_c = -A/T + BT + C, \tag{14}$$

and with this (13) becomes

$$M = \gamma\left[A\left\{\frac{v\pi_c}{pT^2} - \frac{v'\pi'_c}{p'T'^2}\right\} + B\left\{\frac{v\pi_c}{p} - \frac{v'\pi'_c}{p'}\right\}\right]. \tag{15}$$

If the pressure is measured in atmospheres

$$A = 1{\cdot}68 \quad \text{and} \quad B = 8{\cdot}93 \times 10^{-5}.$$

For the special case when $v' = v$ (13) can be written

$$M = \gamma v\left[\left(\frac{A}{T^2} + B\right)\frac{\pi_c}{p} - \left(\frac{A}{T'^2} + B\right)\frac{\pi'_c}{p'}\right]. \tag{16}$$

If M turns out to be positive, it will give the amount of solid CO_2 in kg./hr. accumulated in a section of the regenerator in which the warm gas is cooled and the cold gas heated by 1°.

The numerical calculation shows that, with customary values of v, v', p, p' and $(T - T')$, there will be a certain temperature above which the regenerator will be completely self-purging and below which it will not.

The lower the temperature, the smaller the temperature difference $T-T'$ of the two streams will have to be to enable complete purging to take place. This is shown in Fig. 67 where the maximum values of $T-T'$ are plotted as a function of T' (the lower of the two temperatures) for various values of $pv'/p'v$.

In a modern air-separating plant, the cold nitrogen enters the

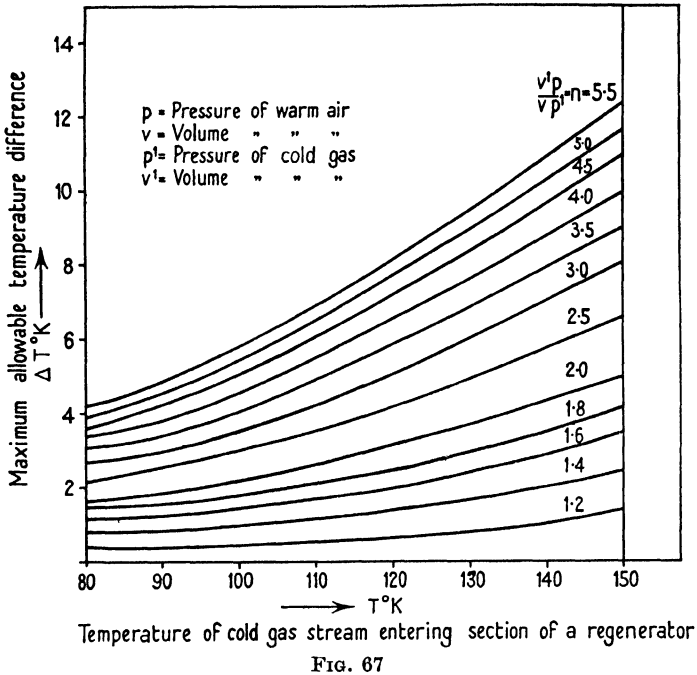


FIG. 67

regenerator at about 90° K. and the ratio p/p' is about 5·5. The figure shows that, if $v' = v$, complete purging will not occur if the temperature difference at the cold end of the regenerators is greater than 4·8° C., whereas in practice it is slightly higher. Actually the conditions are rather less rigorous since, at points where the regenerator is self-purging, the cold gas is not saturated with CO_2. In the Linde–Fränkl plants described in Chapter VII, the difficulty is overcome by arranging for v' to be slightly greater than v.

A similar calculation shows that the elimination of water vapour in regenerator plant involves rather less stringent conditions than are imposed in the case of CO_2.

IV

HEAT, WORK, AND ENTROPY

1. The concept of balance

CONSIDER a gas-separating plant, consisting of one or more of the units described in the last chapter, and suppose a continuous process to be taking place inside it. This process will involve a continuous transfer of matter and heat from one phase to another. It is one of our objects to study this transfer of matter and heat and to determine the laws according to which it occurs. The processes taking place within the plant require the performance of work, generally outside the actual apparatus. This work assumes the form of a compression of the gaseous mixture before it enters the separating units. This expenditure of work is the principal factor in the cost of gas separation and determines, to a great extent, the ultimate price of the pure gases. It is therefore important to conduct the process in such a way as to entail as little work as possible.

It will be shown that the expenditure of a certain amount of work is essential for every separating process, but the work performed in practice is always very much greater than this minimum figure. Part of this 'additional' work is due to frictional losses and imperfect cooling in the compressors and has nothing to do with the construction of the separating units themselves. But a very great portion must be ascribed to processes occurring inside the apparatus. It will be shown that a definite relation exists between every process occurring in some part of the separating plant and the amount of 'additional' work that this process entails, over and above the work that would in any case be necessary to effect a separation of the mixture.

After the plant has been cooled down and the separation has begun, a stationary state is reached in which the gaseous mixture enters and the separated products leave at a constant rate, while no further changes occur in the apparatus itself. In the stationary state, not only the plant as a whole, but all its parts are completely independent of time. This condition gives rise to a number of important laws, which are usually expressed by so-called *balance equations*. These equations are very useful in studying the processes occurring in separating plants.

Balance of mass and composition. Suppose in a given time m moles of mixture enter the plant and m_p, m_q, m_r,... moles leave it as products of separation. In the stationary state there can be no accumulation of

matter in the plant; the total amount of matter leaving must be equal to the total amount entering. This gives the equation

$$m = m_p + m_q + m_r + \ldots, \tag{1}$$

which is known as the 'balance of mass'. Equation (1) is valid, not only for the whole plant but for any one of its parts. If m_a moles of some mixture and m_b moles of another mixture enter some part of the plant in the given time, and if m_p moles of a third mixture and m_q moles of a fourth leave this part in the same time, then

$$m_a + m_b = m_p + m_q. \tag{1'}$$

What is true of the mixture as a whole is also true of any of its components, none of which can accumulate anywhere when the plant is in a stationary state. If, in the mixture of mass m entering, the concentration of one of the components is x, the total amount of this component entering in the given time will be mx. If m is separated into m_p and m_q, which may contain concentrations x_p and x_q of the component in question, the total amount of this component leaving the plant will be $m_p x_p + m_q x_q$, and this must be equal to the total amount of the same component entering. This gives the equation

$$mx = m_p x_p + m_q x_q, \tag{2}$$

which is known as the 'balance of composition'. Clearly equation (2) is not limited to two separation products. The masses may be measured in moles or in units of volume or weight, the concentrations correspondingly in mole fractions, volume fractions, or weight fractions, or, of course, in the corresponding percentages.

Balance of heat. Consider any part of the plant together with the matter it contains at any moment, and suppose that it is adiabatic, meaning that no heat is given off to or absorbed from other parts or the surrounding medium. Suppose also that the only work done in this part is done by or on the atmosphere. A certain quantity of matter enters in the given time and the same quantity leaves. Let the specific† internal energy of the matter entering be u', its specific volume v', and its pressure p'. Similarly, let the specific energy and volume and the pressure of the matter leaving be u'', v'', and p'' respectively. In general, several mixtures will enter and leave at different points, and the equations will not be limited to two terms. Now if Δu be the increase in specific energy incurred by the substances in passing this particular part of the plant, and w the amount of work done on the substances per

† Here and in future a 'specific' quantity will be taken as meaning the value of that quantity for the unit of 'mass', in whatever units the 'mass' is measured. In general, this will be moles. Specific quantities will be denoted by small letters.

unit of mass, then, for an adiabatic process, the first law of thermodynamics gives $\Delta u - w = 0$. Hence

$$u'' - u' + p''v'' - p'v' - \int p\,dv = 0,$$

or, since $\int p\,dv = 0$, $\qquad u' + p'v' = u'' + p''v''$.

Now the expression $u + pv$ is the specific total heat or enthalpy h, so that we may write $h' = h''$. Thus, if a number of mixtures of masses m_a, m_b, m_c,... with specific enthalpies h_a, h_b, h_c,... enter a part of the apparatus, and the masses m_p, m_q, m_r,... with specific enthalpies h_p, h_q, h_r,... leave, we may write the equation

$$m_a h_a + m_b h_b + m_c h_c + \ldots = m_p h_p + m_q h_q + m_r h_r + \ldots, \qquad (3)$$

which may be called the 'balance of heat'.

If the process occurring in this part of the apparatus is not adiabatic, i.e. if a quantity of heat Q is introduced from outside, the equation expressing the balance of heat takes the form

$$m_a h_a + m_b h_b + \ldots + Q = m_p h_p + m_q h_q + \ldots . \qquad (3')$$

Here for the first time we meet with an equation in which a quantity of heat Q is added to an enthalpy H $(= mh)$, a practice that will be very useful in future calculations. Physically it implies the equivalence of 'heat' and 'enthalpy'. In this conception 'heat' may enter and leave an apparatus in two ways, either by conduction or radiation, as expressed by the term Q, or in the form of matter flowing in and out and carrying with it a definite amount of enthalpy mh.

Balance of entropy. Suppose that the process occurring in some part of our plant is reversible as well as adiabatic. In this case, as we know from the second law of thermodynamics, the entropy of the substances leaving this part will be the same as that of those entering. If s_a, s_b,... be the specific entropies of the substances entering, and s_p, s_q,... the specific entropies of the substances leaving, we obtain the following equation, expressing the balance of entropy:

$$m_a s_a + m_b s_b + \ldots = m_p s_p + m_q s_q + \ldots . \qquad (4)$$

If the process is reversible but not adiabatic, i.e. if a quantity of heat Q is introduced from outside, this will entail an increase in entropy equal to Q/T, if T is the temperature of that part of the plant where the heat is introduced. In order that the total entropy in the part considered may remain unchanged, the substances leaving must carry with them more entropy than those entering by an amount Q/T. In this case equation (4) assumes the form

$$m_a s_a + m_b s_b + \ldots + Q/T = m_p s_p + m_q s_q + \ldots . \qquad (4')$$

If, in addition to the introduction of heat from the outside, the process occurring in this part of the apparatus is irreversible, this will entail a further increase in entropy ΔS_{irr}, so that the entropy carried away by the substances leaving the system will have to be greater still in order to maintain the stationary state. In this general case we may write equation (4) as follows:

$$m_a s_a + m_b s_b + \ldots + Q/T + \Delta S_{\text{irr}} = m_p s_p + m_q s_q + \ldots . \qquad (4'')$$

The significance of this irreversible change of entropy will be considered later.

2. The (h, x) diagram

Mass, composition, enthalpy, and entropy are the principal quantities which, together with temperature and pressure, determine the processes of gas separation. To obtain a graphical representation of these processes for the case of air, Keesom† made use of the (h, s, x) surface and its projections on the (h, x) and (h, s) planes. Keesom's theoretical work on air has laid down the general line of research as regards the separation of binary mixtures.

Consider first the (h, x) projection. This diagram will contain a dew-curve and a boiling-curve like the (T, x) and (p, x) diagrams we have discussed in Chapter II. Every point on the dew-curve will have a corresponding point on the boiling-curve such that a liquid and a vapour whose states are defined by these points are in equilibrium with each other. The lines joining corresponding points, which, as in the case of (p, x) and (T, x) diagrams, are known as connodals, will no longer be parallel to the x-axis, since a liquid and a vapour in equilibrium do not possess the same enthalpy; neither will they be perpendicular to the x-axis, as the liquid and the vapour will not have the same composition, except in the two limiting cases of $x = 0$ and $x = 1$. The area between the boiling-curve and the dew-curve will again be called the inhomogeneous region.

Since the enthalpy h of each pure component contains an arbitrary constant, the whole (h, x) diagram may be freely sheared along the h-axis, e.g. by maintaining the scale for $x = 0$ and adding on a constant to the values of h for $x = 1$.

The (h, x) diagram for a binary mixture, containing dew-curve, boiling-curve, connodals, and the isothermals in the superheated region, can be constructed for a given pressure if the properties of the pure components

† W. H. Keesom, *Leiden Commn.*, Suppl. 69 *a*; *Actes du VI^ème Congrès International du Froid*, Buenos Aires, 1932: *Rapport de la I^ère commission*, p. 136.

are known together with certain data referring to the mixture itself. In the general case it would be necessary to know the equilibrium (T, x) or (p, x) curves, the specific heat of the gas phase as a function of temperature and pressure, and either the heat of mixing or the latent heat of vaporization of the mixture. In the case of a perfect solution, as was shown in Chapter II, the equilibrium curves can be calculated and

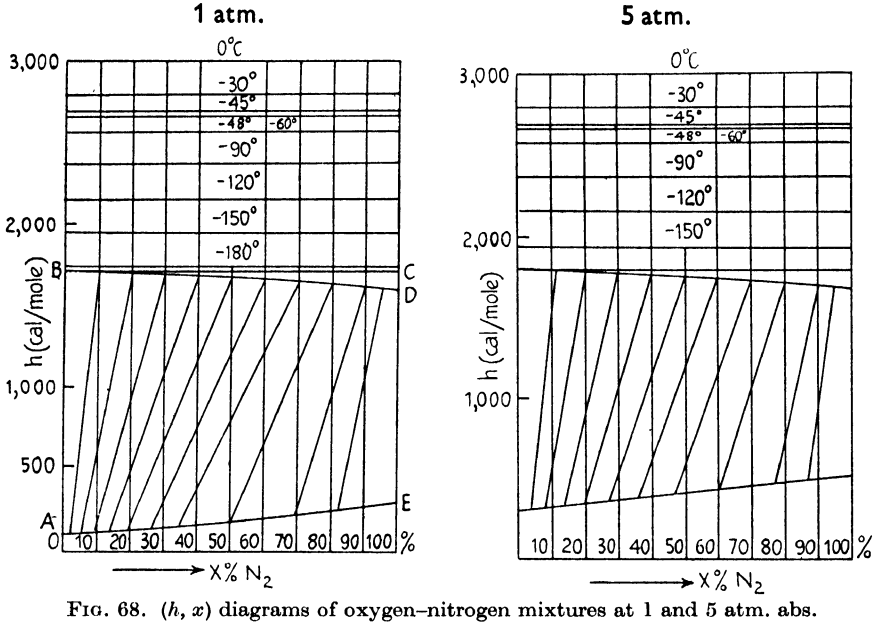


FIG. 68. (h, x) diagrams of oxygen–nitrogen mixtures at 1 and 5 atm. abs.

expressed in terms of the 'k-values' of the individual components. No heats of mixing have as yet been measured for substances with boiling-points at low temperatures. Latent heats of vaporization, which will be considered in some detail in the succeeding section, have been determined only for mixtures of oxygen and nitrogen† and, on the basis of these measurements, Keesom and Tuyn‡ have constructed (h, x) diagrams for this system at 1 and 5 atm. abs. These are reproduced in Fig. 68. Tables 10 and 11 give the values of h in cal./mole for the dew- and boiling-curves at 1 and 5 atm.

The (h, x) diagram for 1 atm. was constructed as follows. First the specific enthalpy of liquid oxygen is chosen as 100 cal./mole at the boiling-point at 1 atm. pressure. This gives point A in Fig. 68. The corresponding point B on the dew-curve is obtained by adding the latent

† L. I. Dana, *Proc. Amer. Acad.* **60**, 241 (1925).

‡ W. H. Keesom and W. Tuyn, *Actes du VI^ième Congrès International du Froid*, Buenos Aires, 1932: *Rapport de la I^ère commission*, p. 174.

TABLE 10. *Specific Enthalpy h in cal./mole for O_2–N_2 Mixtures at 1 atm. along Dew-curve and Boiling-curve*

Mole % N_2	*Vapour*	*Liquid*
0	1,732	100
10	1,727	110
20	1,722	124
30	1,716	143
40	1,708	163
50	1,700	186
60	1,692	210
70	1,682	235
80	1,670	259
90	1,656	282
95	1,649	294
100	1,641	304

TABLE 11. *Specific Enthalpy h in cal./mole for O_2–N_2 Mixtures at 5 atm. along Dew-curve and Boiling-curve*

Mole % N_2	*Vapour*	*Liquid*
0	1,800	314
10	1,793	335
20	1,786	358
30	1,779	380
40	1,771	400
50	1,762	420
60	1,753	442
70	1,743	465
80	1,732	490
90	1,720	514
95	1,713	526
100	1,707	537

heat of evaporation of pure oxygen (1,632 cal./mole) to the ordinate of point A. The arbitrary constant in the enthalpy of nitrogen is then fixed by making the enthalpy of pure gaseous nitrogen at the boiling-point of oxygen equal to the enthalpy of pure oxygen vapour at this temperature, i.e. 1,732 cal./mole. This determines a point C on the nitrogen axis at the same height as B. With the assumption that the enthalpy of a gaseous mixture is a linear function of the enthalpies of the pure components, the isothermal through B and C becomes a straight line parallel to the x-axis. The dew-curve in the (h, x) diagram is then determined by subtracting from 1,732 cal./mole the value of $\int_T^{90\,1} C_p\, dT$ at various compositions. The lower limit T of the integral is taken from the (T, x) diagram. The specific heats of the mixture can be obtained from those of the pure components, since the additivity of enthalpies in the gas implies that of specific heats also. The isothermals in the homogeneous region above the dew-curve can be obtained in the same way. The enthalpy of liquid nitrogen at the boiling-point is then determined by subtracting 1,337 cal./mole, the latent heat of evaporation of nitrogen, from point D at the end of the vapour-curve. This gives point E in Fig. 68. To compute the boiling-curve, the heats of evaporation of the mixture at various concentrations must be known, since there is no justification for assuming additivity of enthalpies in the liquid. We shall treat these heats of evaporation separately in the next section. For oxygen–nitrogen mixtures at atmospheric pressure, Dana† determined heats of evaporation, giving the vertical distances between

† L. I. Dana, loc. cit.

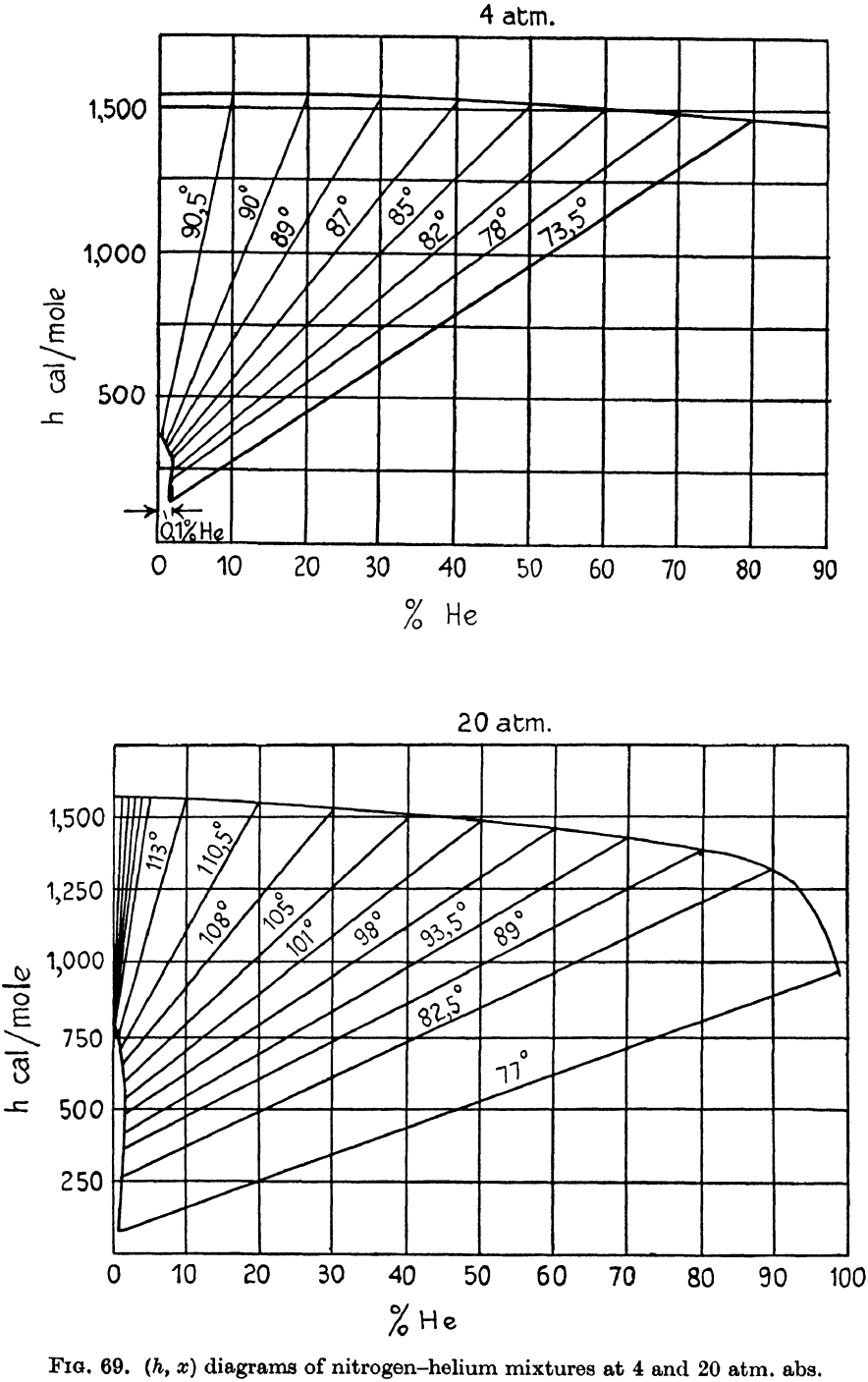


FIG. 69. (h, x) diagrams of nitrogen–helium mixtures at 4 and 20 atm. abs.

points on the dew-curve and boiling-curve. Thus the boiling-curve may be drawn. The connodals can then be inserted from the (T, x) curves.

The diagram for 5 atm. was determined from that at 1 atm. with the help of the known pressure dependence of the properties of the pure components.

It must be pointed out that, in assessing the specific heats of the gaseous mixtures from those of the pure substances, in order to obtain the dew-curve at any pressure, it is always necessary to ascribe a value to the specific heat of one component under conditions at which it cannot exist as a gas. For the dew-point temperature of the binary mixture lies below that of one of the constituents. At low pressures, where the specific heat of the gas is relatively independent of temperature and pressure, the extrapolation can be performed without much risk, but at higher pressures, and especially in the neighbourhood of the critical pressure of the component, we come up against serious difficulties, which can be overcome only by an experimental determination of the specific heat of the mixture. Similar difficulties are encountered if we try to fix the boiling-curve first with the help of the specific heats of the liquid mixtures.

Fedoritenko and Ruhemann† constructed (h, x) diagrams for mixtures of nitrogen and helium at 4 and 20 atm. These are shown in Fig. 69. In this case the heats of vaporization of the mixture were not known, but the solubility of helium in liquid nitrogen is so small that the latent heat of pure nitrogen can be used without serious error.

3. Heats of evaporation of binary mixtures

The heat required to evaporate a liquid mixture and the heat given off when a gaseous mixture is condensed differ according to the conditions under which the process is carried out. V. Fischer‡ was the first to define these various kinds of latent heats and to point out relations connecting one with another.

If a liquid mixture is completely evaporated at constant pressure, the final vapour will have the same composition x as the initial liquid, though both will have different compositions at an intermediate stage of the process. The heat so absorbed is clearly the difference between the enthalpy of the vapour and that of the liquid taken at the same pressure and the same composition, and since enthalpy is a function of the state of the substance, this difference must be independent of the path traversed by the mixture between the initial and the final state.

† A. Fedoritenko and M. Ruhemann, *Tech. Phys. U.S.S.R.* **4**, 1 (1937).

‡ V. Fischer, *Ann. der Physik* (5), **17**, 209 (1933).

ıe difference between these two enthalpies is called λ_{px} and is known the integral heat of vaporization of the mixture at constant pressure. n the (h, x) diagram, λ_{px} is the vertical distance between a point on e dew-curve and a point on the boiling-curve immediately beneath it. should be noted that, in general, the temperature will not remain ınstant during this process, since not the vertical lines but the sloping ınnodals are the isothermals in the inhomogeneous region.

However, the mixture can also be evaporated at constant tempera- ıre and variable pressure. The latent heat will now be λ_{Tx}, the integral

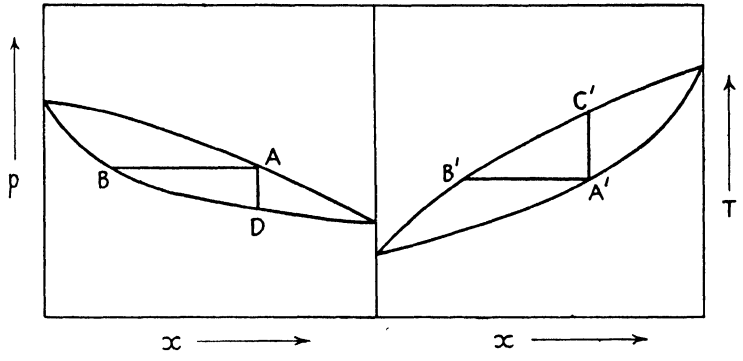


FIG. 70. (p, x) and (T, x) diagram to illustrate different latent heats of evaporation

ɜat of vaporization at constant temperature and composition, and $_x$ will in general be different from λ_{px}. λ_{Tx} does not appear on the $, x)$ diagram as the difference of two enthalpies, since dew-curves and ɔiling-curves are drawn for constant pressure and not for constant ɜmperature. λ_{Tx} is the difference between the enthalpy at point D of dew-curve and point A of a boiling-curve on a (p, x) diagram as shown ı Fig. 70, while λ_{px} is the difference between the enthalpies at C' and $'$ on the (T, x) diagram in the same figure. If a number of (h, x) curves ır various constant pressures are plotted on the same (p, x) diagram, $_x$ will appear as the vertical distance from a point on a boiling-curve ır one pressure and a point immediately above it on a dew-curve for lower pressure, the dew-point of the latter having the same tempera- ıre as the boiling-point of the former. The mixture will have to be ɛpanded during evaporation to keep the temperature from rising ɜtween the boiling-point and the dew-point.

Suppose 1 mole of vapour to be formed from so large a reservoir of ɥuid that the composition of the latter does not alter appreciably ıring the operation. Thus the vapour formed will be in equilibrium ith this liquid and will then have a different composition from the

liquid. The two points on the (p, x) diagram (A, B in Fig. 70) will lie at the ends of a connodal and the heat absorbed is known as λ_{vl}, the differential heat of evaporation.

It can be shown at once that λ_{vl} is not the difference between the enthalpy h'' of the vapour at B and the enthalpy h' of the liquid at A. Enthalpy is defined only as a difference, and it was seen in the last paragraph that the zero point of enthalpy could be fixed arbitrarily for each component separately. There is nothing to prevent us, for instance, raising the zero enthalpy for the component with $x = 1$ by an arbitrary amount, say 100 cal., while leaving the zero point of the other pure component unaltered. Then all enthalpies in the figure will rise by an amount $100x$ cal. Evidently vertical distances between two points of the same composition will not change, but the corresponding distances between points with different values of x will alter. It is clear that a latent heat cannot be defined in such a way as to make it depend on the system of coordinates. It will be shown presently how λ_{vl} can be evaluated correctly.

If 1 mole of liquid is formed from a very large quantity of gas, it will be in equilibrium with the gas and will again be described by a point at the end of a connodal through the corresponding vapour point. This will give rise to a differential heat of condensation λ_{lv}, but the value of $-\lambda_{lv}$ will in general not be the same as λ_{vl} because the moles of mixture changing from one phase to the other have different compositions in the two processes. In the case of λ_{vl} the composition of this mole of mixture was that of the vapour; in the case of $-\lambda_{lv}$ it is that of the liquid in equilibrium with this vapour. Just as in the former case, $-\lambda_{lv}$ is not the difference between the enthalpies at points B and A on Fig. 70.

To evaluate these latent heats, it is best to make use of the partial molar enthalpies h_A and h_B of the components A and B in a binary mixture, which are defined as

$$h_A = \left(\frac{\partial H_A}{\partial n_A}\right)_{pTn_B}; \qquad h_B = \left(\frac{\partial H_B}{\partial n_B}\right)_{pTn_A}. \tag{5}$$

Just as in Chapter II, p. 28, a relationship was derived between the Gibbs potential G and the chemical potentials μ_i, we can derive a similar relationship between the total enthalpy H or the specific enthalpy h (based on 1 mole of mixture) and the partial molar enthalpies h_A and h_B. This can be written

$$H = n_A h_A + n_B h_B \quad \text{or} \quad h = x_A h_A + x_B h_B. \tag{6}$$

Moreover, if A is the component whose concentration is x, it can be

shown that

$$h_A = h+(1-x)\frac{\partial h}{\partial x}, \tag{7}$$

$$h_B = h-x\frac{\partial h}{\partial x}. \tag{8}$$

In the following the concentration of component A will be called x in the liquid and z in the vapour. Liquid enthalpies will be marked with a $'$ and gaseous enthalpies with $''$.

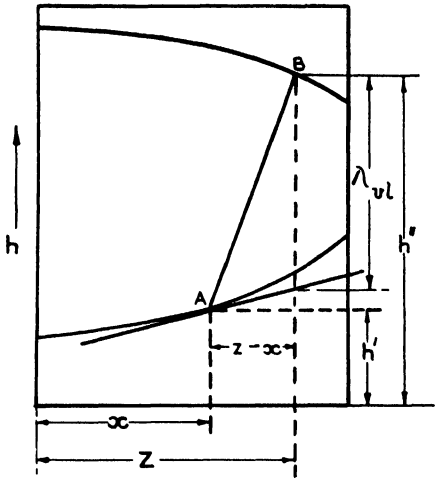


FIG. 71. Determination of λ_{vl}

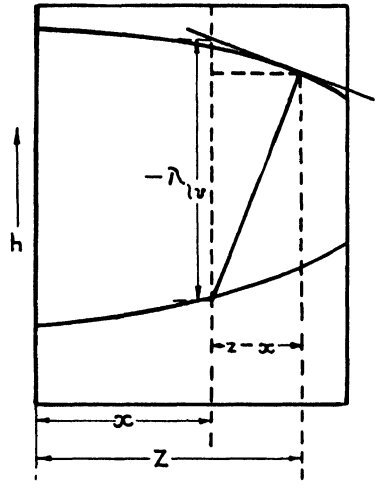


FIG. 72. Determination of $-\lambda_{lv}$

Now in the evaporation of 1 mole from a large quantity of liquid with composition x_A, the enthalpy of the vapour phase increases by

$$zh''_A+(1-z)h''_B$$

and that of the liquid decreases by

$$zh'_A+(1-z)h'_B.$$

Hence $$\lambda_{vl} = z(h''_A-h'_A)+(1-z)(h''_B-h'_B).$$

Inserting (7) and (8) in this equation

$$\lambda_{vl} = z\left\{h''+(1-z)\frac{\partial h''}{\partial z}-h'-(1-x)\frac{\partial h'}{\partial x}\right\}+(1-z)\left\{h''-z\frac{\partial h''}{\partial z}-h'+x\frac{\partial h'}{\partial x}\right\},$$

whence $$\lambda_{vl} = h''-h'-(z-x)\frac{\partial h'}{\partial x}. \tag{9}$$

Thus by drawing a tangent to the boiling-curve λ_{vl} can be read off the (h, x) diagram as shown in Fig. 71.

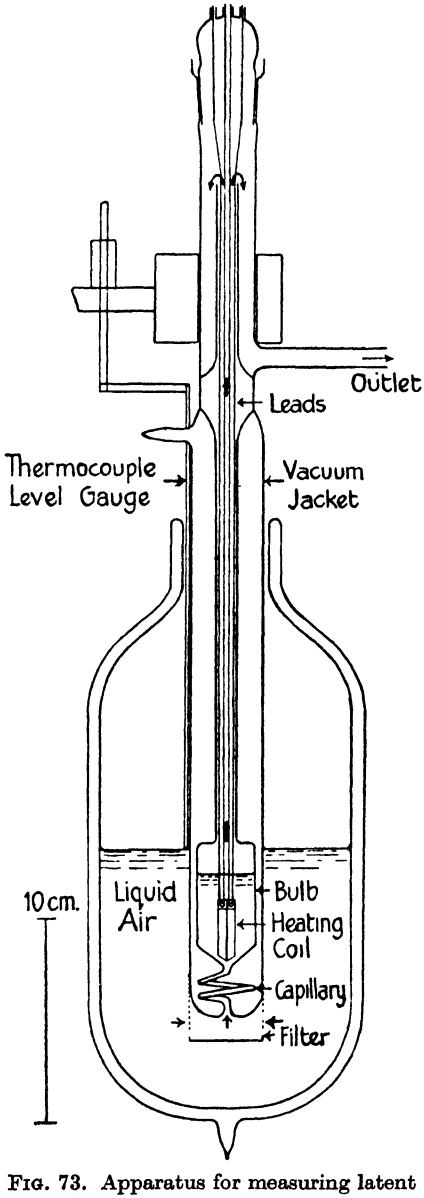


FIG. 73. Apparatus for measuring latent heats λ_{px} of binary mixtures at constant pressure and constant composition

In exactly the same way, we can find for $-\lambda_{lv}$

$$-\lambda_{lv} = h''-h'-(z-x)\frac{\partial h''}{\partial z}, \quad (10)$$

which can therefore be read off the (h, x) diagram by drawing a tangent to the dew-curve as shown in Fig. 72.

Of the various latent heats here defined only λ_{px} has been determined experimentally. Dana† succeeded in measuring the latent heat of oxygen–nitrogen mixtures at atmospheric pressure. With an electric heating coil the liquid mixtures were evaporated from an insulated glass vessel, liquid of constant composition being continuously introduced into this calorimeter. In the stationary state the vapour leaving the apparatus must have the same composition as the liquid introduced. At the same time the liquid in the calorimeter will be enriched with oxygen, so as to be in equilibrium with the escaping vapour. But this liquid does not enter into the process. From the quantity of heat introduced and the amount of vapour leaving the apparatus in a given time, λ_{px} is obtained for the composition of the escaping vapour. Fig. 73 shows a sketch of Dana's apparatus. Fig. 74 gives λ_{px} as a function of the composition.

As has been mentioned, heats of evaporation of other binary mixtures are deplorably lacking and no determinations have as yet been made at higher pressures.

† L. I. Dana, loc. cit.

4. Calculations on the (h, x) diagram

The (h, x) diagram enables us to calculate effects connected with the transport of heat and matter simultaneously. In order to facilitate these calculations, Keesom† introduced a simple analytic method which allows relations involving balance of heat and balance of mass and composition to be expressed in a single equation.

At first we shall confine ourselves to processes occurring at constant pressure. A binary mixture in a certain state, which may be denoted

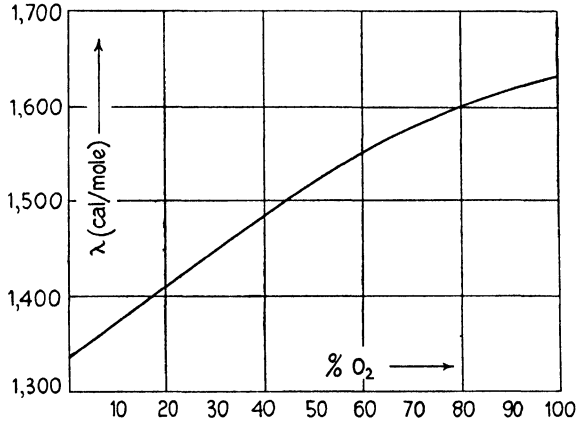


FIG. 74. Latent heat λ_{px} at constant pressure and constant composition of oxygen–nitrogen mixtures at atmospheric pressure

by a point A on the (h, x) plane, is termed a phase. A phase A is considered to have three properties, a mass m_A, a composition x_A, and a specific enthalpy h_A. Whereas x_A and h_A are represented by the coordinates of the point A on the (h, x) plane, m_A is not represented.

Now suppose two mixtures, having different compositions and enthalpies, which are represented by two points on the (h, x) plane, to be brought together and mixed. The resulting mixture will obviously have a mass equal to the sum of the masses of the two original mixtures. The resulting composition and enthalpy will be represented by a point on the (h, x) plane situated on the straight line joining the first two points at the centre of gravity of the masses at these points (see Fig. 75).

Moreover, if from m_A moles of a mixture A with a composition x_A and a specific enthalpy h_A we remove a quantity m_B, having a composition x_B and a specific enthalpy h_B, the remainder, which may

† W. H. Keesom, *Leiden Commn.*, Suppl. 69 *a*; *Proc. Amsterdam*, **33**, 901 (1930); *Actes du VI*ième *Congrès International du Froid*, 1932: *Rapport de la I*ère *commission*, p. 136.

contain m_C moles with the coordinates x_C and h_C, will be represented by a point C on the projection of the straight line AB such that A lies at the centre of gravity of B and C. If we bring a mixture C to a point of the (h, x) plane situated in the inhomogeneous region for the pressure in question (see Fig. 76), we know that this mixture will separate into a liquid A and a vapour B, which will be represented on the diagram by two points, one on the dew-curve and one on the boiling-curve. They will lie on a straight line (the connodal) through C, and the relative quantities of liquid and vapour will be such that C is the centre

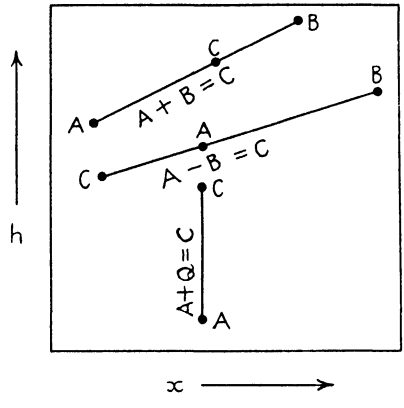


FIG. 75. Addition and subtraction of phases

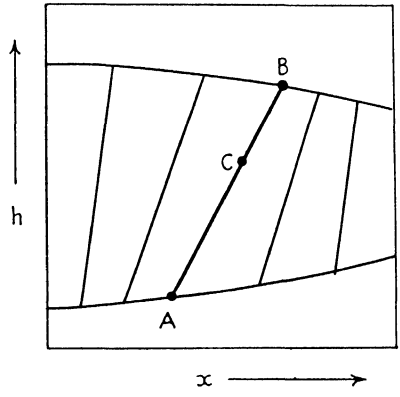


FIG. 76. State in inhomogeneous region as 'sum' of liquid and vapour phase

of gravity of A and B. Finally, if a quantity of heat Q be introduced to a phase A, mass and composition of the phase will remain unchanged, while its specific enthalpy h_A will be increased by an amount Q/m_A (see Fig. 75).

Keesom expresses these obvious physical facts analytically in the following way. A phase C is defined as the sum or difference of two phases A and B, expressed by the equation $A \pm B = C$, if the following equations hold:

$$\left.\begin{aligned} m_A \pm m_B &= m_C \\ m_A x_A \pm m_B x_B &= m_C x_C \\ m_A h_A \pm m_B h_B &= m_C h_C \end{aligned}\right\}. \tag{11}$$

A phase C is said to be the sum or difference of a phase A and a quantity of heat Q, expressed by the equation $A \pm Q = C$, if the following equations hold:

$$\left.\begin{aligned} m_A &= m_C \\ x_A &= x_C \\ h_A \pm Q/m_A &= h_C \end{aligned}\right\}. \tag{12}$$

These equations express analytically just those geometrical relations which we have described.

To illustrate the practical use of this method we shall take a simple example of a problem of gas separation. Suppose that in a certain time 1 ton of a binary mixture, having a given temperature and pressure, is to be separated into components of specified purity. Suppose that one of these products is to be obtained as a saturated vapour, the other as a boiling liquid. How the separation is to be effected is of no im-

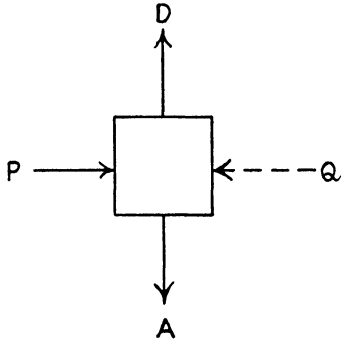


FIG. 77. Schematical separating process

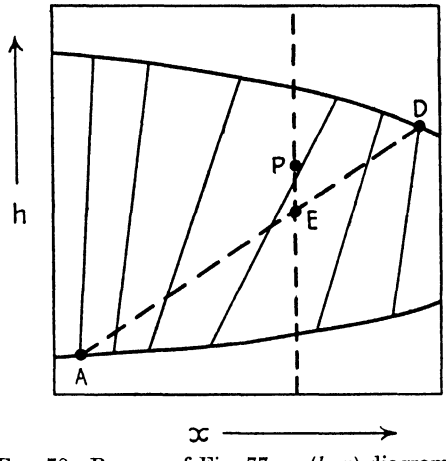


FIG. 78. Process of Fig. 77 on (h, x) diagram illustrating use of Keesom's method

portance, but we are asked to find how much heat is given off or absorbed in the course of the process.

In Fig. 77 the process is illustrated schematically: a phase P enters the separator, a gas D and a liquid A leave it in the same period of time. Simultaneously a quantity of heat Q (positive or negative) is absorbed.

Now consider the process on the (h, x) diagram (Fig. 78). Suppose P is a mixture partly gaseous, partly liquid. As its temperature and composition are known we can plot the point on the figure. Similarly, we can plot A and D as we know their compositions and that they are situated on the equilibrium curves.

The balance equation for this process is, according to our algebra,

$$A+D = P+Q.$$

Let

$$A+D = E.$$

Then, according to equations (11) and (12), E is on the straight line AD

with a composition equal to that of P, and the vertical distance PE is equal to the value of Q we are seeking. Since in the figure h_P is greater than h_E, Q is negative, that is to say, heat must be withdrawn from the system.

In some cases it may be useful to consider on one (h, x) diagram a process occurring at variable pressure. We may, for instance, plot a series of boundary curves, each valid for a definite pressure; but if we insert all the connodals, the figure will tend to become unreadable.

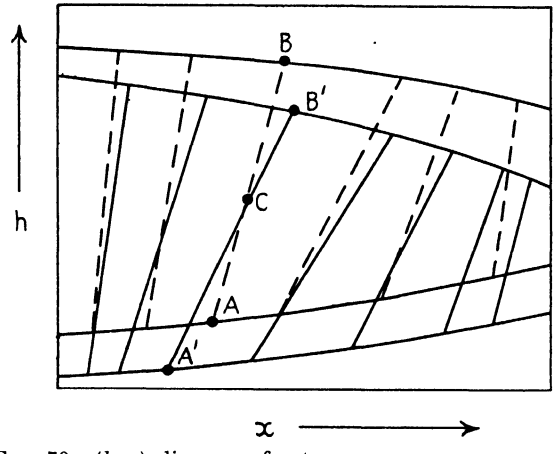


FIG. 79. (h, x) diagrams for two pressures superposed, showing the result of a change at constant enthalpy on the amount and composition of liquid and vapour phases

However, one example of the use of one diagram for two pressures may be interesting. In Fig. 79 the boundary curves and a few connodals are given of some mixture, say at 5 atm. and at 1 atm. Suppose a liquid A and a vapour B to be in equilibrium at 5 atm. A and B will lie at the ends of a connodal. The phase characterizing the sum of these two mixtures will lie on the connodal at a point C, and the ratio $AC:BC$ will be determined from the quantity of gas and liquid present. Now suppose the two equilibrium mixtures to be expanded in a valve to 1 atm. Under these circumstances the total mass and the total composition of phase C will, of course, remain unchanged. Moreover, the enthalpy h_C will also remain unchanged. On an (h, x) diagram describing states of 1 atm. and 5 atm. simultaneously, point C will therefore not move as a result of the expansion. However, the liquid and vapour in equilibrium after the expansion will not be represented by the same points A and B. These points will shift to A' and B' at the ends of the connodal for 1 atm. through C. Thus the compositions of the

two phases, as well as their enthalpies, taken separately, will change. Similarly, as the ratios $AC:BC$ and $A'C:B'C$ will in general not be the same, the amount of liquid and the amount of gas present will not be the same after and before the expansion.

A further example, taken directly from a problem of gas separation, brings out still more clearly the uses of Keesom's symbolic algebra. Consider a portion of a rectifying column such that a liquid is introduced from above and a vapour from below (Fig. 80). Inside the column there will be some kind of interaction between the liquid and the vapour, which we need not specify for the present, and finally a vapour will emerge at the top and a liquid at the bottom. We shall suppose that no heat enters from outside and that the state is stationary.

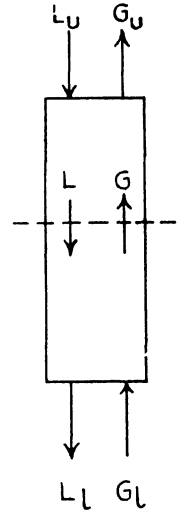


FIG. 80. Portion of rectifying column (schematical) illustrating equivalent current

We can now apply the balance equations developed in the last paragraph and, with our symbolic algebra, we can write down the balance of mass, composition, and heat in a single equation as in the last example.

Let the suffix u refer to the top of the apparatus and the suffix l to the bottom. Then the liquid entering above will be L_u and that leaving below will be L_l. Similarly, G_u is the vapour leaving at the top and G_l the vapour entering at the bottom. Then

$$L_u+G_l = L_l+G_u,$$

or

$$L_u-G_u = L_l-G_l = Z.$$

On the (h, x) diagram Z is the point of intersection of the straight lines through L_u, G_u and L_l, G_l, as shown in Fig. 81. Now, if we consider any horizontal section of the apparatus and determine the amount, composition, and enthalpy of the liquid and vapour entering and leaving this section in a given time, we shall obtain exactly the same equations. The difference between the liquid and gaseous 'phases' entering the section will be equal to the difference between the liquid and gaseous phases leaving the section and will in turn be equal to Z. The phase Z is usually known as the equivalent down-current, and we may sum up our results by saying that the equivalent down-current remains unchanged throughout any adiabatic piece of apparatus in so far as no substances are admitted or withdrawn on the way. The phase

$$G-L = R = -Z$$

is called the equivalent up-current and is, of course, similarly a constant.

It is customary to choose equivalent phases the masses of which are positive. Accordingly, if more liquid flows down than vapour flows up, we shall speak of an equivalent down-current and vice versa. As these equivalent currents are mathematical definitions and as such not bound to have physical significance, we need not be surprised if we occasionally come upon such currents with concentrations less than 0 or greater than 1 or with negative enthalpies. We may be sure that all phases actually emerging from the apparatus or present as homogeneous entities will always have 'rational' components.

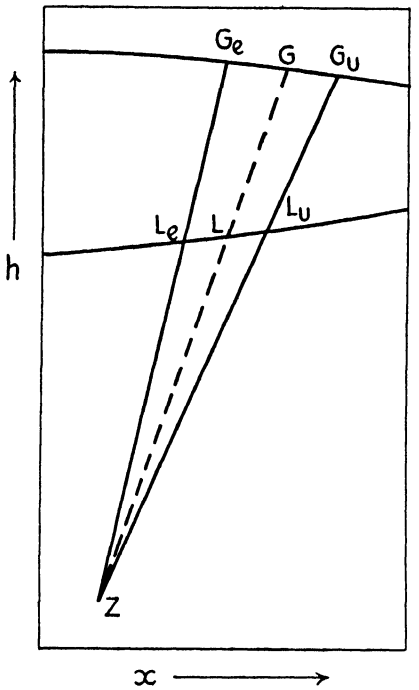


FIG. 81. (h,x) diagram illustrating equivalent current

5. The (h,s) diagram

Keesom and Tuyn† constructed the (h,s) and (s,x) projections of the (h,s,x) surface for oxygen–nitrogen mixtures. For the details of the construction we must refer the reader to the original paper. In Fig. 82, which shows the three projections for 1 atm. pressure, the entropy of boiling liquid oxygen is taken as zero. Then the entropy of saturated pure gaseous oxygen is λ_0/T, where $\lambda_0 = 1{,}632$ cal./mole is the heat of evaporation of oxygen, and $T = 90{\cdot}1°$ K., the boiling-point of oxygen. This gives for the entropy of saturated gaseous oxygen $s_1 = 18{\cdot}11$ cal./deg. mole. The entropy of pure gaseous nitrogen at $90{\cdot}1°$ K., i.e. at the boiling-point of oxygen, is taken as $s_2 = 38{\cdot}11$ cal./deg. mole, which makes $s_2 - s_1 = 20{\cdot}0$ cal./deg. mole.

Before we can begin to use the (h,s) diagram we must remember that the sum and difference of two phases have not been defined for this projection. In equations (11) and (12) of the last section no mention was made of entropy. Now these two sets of equations could be amplified with the help of the balance equations (4)–(4″) in § 1 of this chapter. We could, if we liked, consider a phase as consisting not of three but of four component parts m, x, h, and s, and could define the sum and

† W. H. Keesom and W. Tuyn, loc. cit.

difference of two phases with the help of equations (4)–(4″) so as to include entropy. But if we did this the equations (11) and (12) of the last section would be valid only for isentropic processes. For all other processes, instead of

$$A+B=C,$$

we should have to write

$$A+B+\Delta S=C,$$

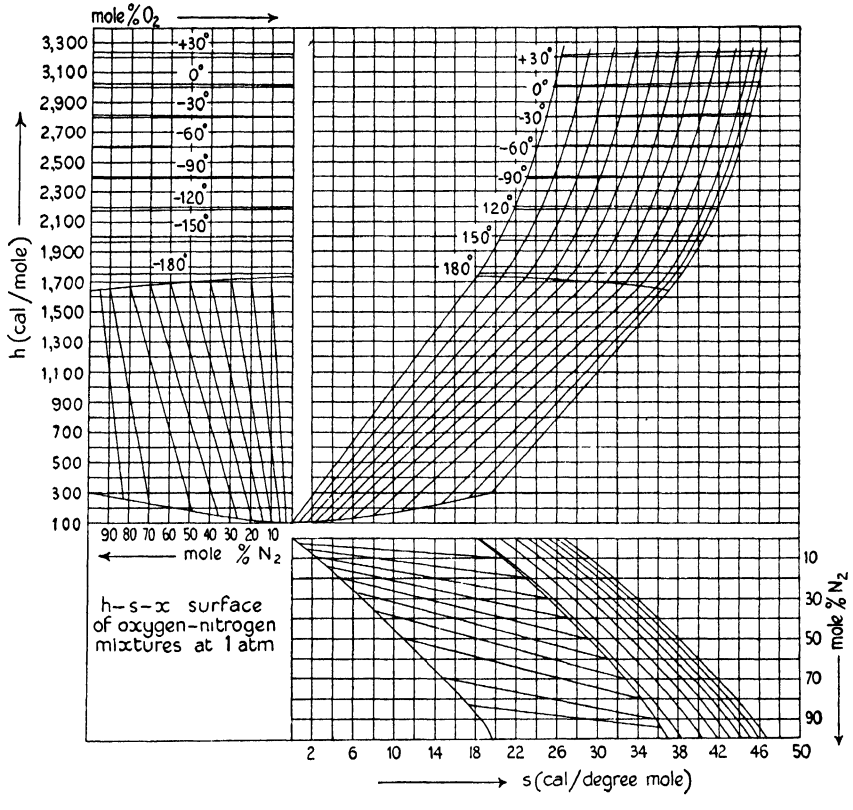


FIG. 82. (h, x), (h, s), and (x, s) projections of the (h, s, x) surface for mixtures of oxygen and nitrogen at 1 atm.

in which ΔS is the increase of entropy occurring in the course of the process. Similarly, the equation

$$A+Q=C$$

would now read $$A+Q+T\,\Delta S=C.$$

This would greatly complicate our calculation, which would thus lose its principal virtue of simplicity.

To understand this clearly we must realize that we have in fact employed the equation $A+B=C$ in two distinct senses:

(1) the two phases A and B may be considered equivalent to a single phase C, which is mathematically defined as their sum;
(2) the two phases A and B will, if brought together, form a single phase C, or, conversely, the phase C will separate into two phases A and B.

(1) is merely a useful mathematical operation, whereas (2) refers to a definite physical occurrence. The whole force of the equation $A \pm B = C$ is that it may have either of these two meanings, that we need not, in applying it, worry whether the two phases really do combine to form a single phase or whether we are simply combining them on paper to simplify our calculations. It is, in fact, quite immaterial for this equation whether the two phases are interacting or, on the contrary, completely isolated from each other. It would be unwise to forgo this advantage by introducing new equations.

Now it is clear that, as long as our two phases are combined simply 'on paper', but in point of fact are not interacting at all, the entropy of their sum will be equal to the sum of their entropies. For this case we can complete equation (11) as follows:

$$\text{if} \quad \left.\begin{aligned} A \pm B &= C \\ m_A \pm m_B &= m_C \\ m_A x_A \pm m_B x_B &= m_C x_C \\ m_A h_A \pm m_B h_B &= m_C h_C \\ m_A s_A \pm m_B s_B &= m_C s_C \end{aligned}\right\}. \qquad (11')$$

In this case a point giving the sum or difference of two phases will lie on the straight line joining the two phase-points (or on its projection) in the (h, s) diagram also. But when the two phases A and B interact, the entropy of the sum will in general differ from the sum of the entropies. The sum and difference of two phases would then not lie on the straight line joining the phase-points, and in this case the equation will not be applied at all. The rules of addition and subtraction will be considered to include entropies *only* when the addition and subtraction is a mathematical combination of two phases that do not interact, but *never* when the sum or difference is considered as the result of interaction.

To make this quite clear let us refer back to the example at the end of the last section (Fig. 80). A liquid L_u enters the top of the column

and a gas G_u leaves. A liquid L_l leaves the bottom and a gas G_l enters at the bottom. We obtained the equation

$$L_u - G_u = L_l - G_l = Z. \tag{13}$$

But since the gases and liquids may, for all we know, interact inside

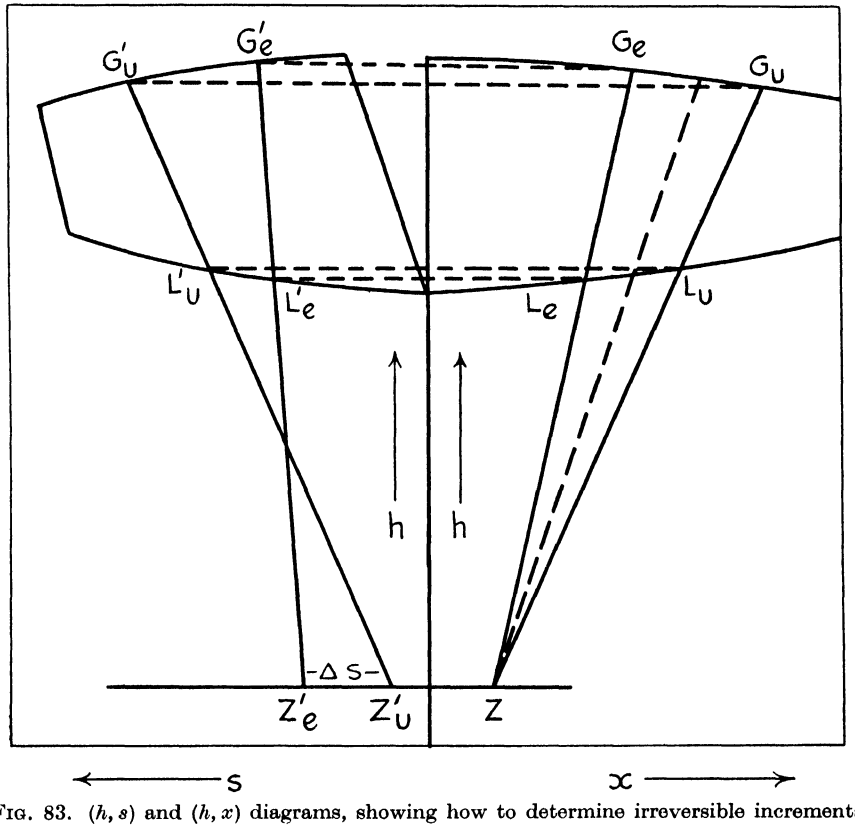


FIG. 83. (h, s) and (h, x) diagrams, showing how to determine irreversible increments of entropy

the apparatus, we may not simply extend the equation to include summation of entropies. However, the differences $L_u - G_u$ and $L_l - G_l$ are simply mathematical combinations. L_u and G_u are two separate phases and if we regard them as a single phase it is merely for convenience. We have not actually mixed them. Thus we may find $L_u - G_u$ and $L_l - G_l$ on the (h, s) diagram by producing the straight lines joining the L's and G's to the ordinate $h = h_Z$. But we must not expect them to meet at these points (see Fig. 83). For equation (13) is not applicable to entropy. *The distance parallel to the s-axis between the points* $L_u - G_u$

and $L_l - G_l$ will, in fact, give us the change in entropy undergone by the equivalent current in passing through the apparatus. Since in our example the process is regarded as adiabatic, this change of entropy must be irreversible. By carrying out this construction at various points of a separating plant we can thus determine the irreversible entropy increase taking place at each point.

6. Net work and irreversible entropy

We shall now derive the relation between the changes of entropy undergone by mixtures in the interior of a separating plant and the work necessary to carry out the separation process. More especially we shall show what part of the total work is inherent in the actual act of separation and what part is due to irreversible changes which could in principle be eliminated by a suitable reconstruction of the plant.

Hausen† has shown how a completely reversible separating plant can at least be conceived. All practical units are more or less successful approximations to this ideal separator. We shall see that, the closer we approximate to a reversible process, the smaller will be the work or, as it is frequently termed, the power input required.

Consider a plant for separating a gaseous mixture, placed in an environment which is at a constant temperature T_0. The mixture may have any number of components, but for simplicity we shall assume that there are only two. Heat may be introduced or withdrawn at any number of points. We shall here assume that a quantity of heat Q (positive or negative) is introduced into the system in a reversible manner. Let us suppose that a stationary state has been reached. We assume that in a given time a volume of gas V_1 is introduced at a pressure p_1 and a volume V_2, consisting of products of separation, is withdrawn at p_2. It will in general be useful to include in what is termed the 'plant' any compressors that take part in the process. Frequently p_1 and p_2 will both be atmospheric pressure, but this is by no means essential.

If W' is the work done *on* the system, which incurs an increase in internal energy ΔU, then

$$W' = \Delta U - Q. \tag{14}$$

Now W' may be of two kinds, work done by the compressors and work done by the atmosphere. We are here interested only in the first item, which is often called the *net work*, since it is only this net work that

† H. Hausen, *Zeits. f. techn. Physik*, **13**, 271 (1932) .

requires an input of power. We shall denote the net work by W.† Since the work done by the atmosphere is $-\Delta pV$,

$$W = W' + \Delta pV = \Delta U + \Delta pV - Q = \Delta H - Q, \tag{15}$$

where ΔH is the difference in enthalpy between the separated gases and the original mixture.

Now let S be the entropy of the plant and all that is in it, and let S_0 be the entropy of the surroundings, which we have assumed to be at a temperature T_0. Then

$$\Delta S + \Delta S_0 \geqslant 0. \tag{16}$$

Since heat exchange with the surroundings is reversible, $\Delta S_0 = -Q/T_0$. Therefore

$$\Delta S \geqslant Q/T_0. \tag{17}$$

If the entire process occurs reversibly, $\Delta S = Q/T_0$, and equation (15) yields

$$W_{\text{rev}} = \Delta H - T_0 \Delta S. \tag{18}$$

This is known as the *reversible work of separation.*

In practice irreversible changes occur in a separating plant. In this case $\Delta S > Q/T_0$ and we may write

$$\Delta S = Q/T_0 + \Delta S_{\text{irr}}. \tag{19}$$

Then $$Q = T_0 \Delta S - T_0 \Delta S_{\text{irr}},$$

and $$W = \Delta H - T_0 \Delta S + T_0 \Delta S_{\text{irr}}, \tag{20}$$

or $$W = W_{\text{rev}} + T_0 \Delta S_{\text{irr}}. \tag{21}$$

We see that every irreversible change of entropy occurring in the apparatus requires the expenditure of an additional amount of work $W_{\text{irr}} = T_0 \Delta S_{\text{irr}}$.

Equations (18), (19), and (20) show us the simple relations that exist between enthalpy, entropy, and the work of separation. By determining the change in enthalpy and entropy, undergone in various parts of the plant, we can calculate the work needed to separate the mixture. Moreover, since the formulae allow us to distinguish between reversible and irreversible entropy changes, we can find out which parts of the apparatus are responsible for the greatest entropy increments and accordingly for an increased power input, as compared with that necessary in an ideal, reversible separating plant.

† In most text-books the net work is called W' and the total work W. It seemed preferable to reverse the terms here as it is the net work that features in all the calculations and is the more important quantity from the point of view of the engineer.

V

REFRIGERATION

1. Refrigeration, liquefaction, and separation

THE withdrawal of heat from a substance which is itself at a lower temperature than its surroundings is known as refrigeration. Every process which takes place below room-temperature requires some form of refrigeration, firstly to produce and secondly to maintain the low temperature.

In the usual form of refrigerator a working substance called the refrigerant is made to absorb heat from another substance, which may be apples or butter, and which is thus maintained at a temperature below that of the surroundings. A certain amount of heat is given off by the refrigerant to the surroundings and a certain amount of work is done on the refrigerant.

The refrigerant is generally a system which is wholly or partly in the gaseous state at room-temperature and atmospheric pressure, and partly or wholly liquid at some point in the refrigerating process. This is because a gas, in view of its great compressibility, can have much work performed upon it without requiring high pressures, and because the transition from a liquid to a vapour and vice versa, in view of the latent heats involved, is coupled with the absorption and delivery of large quantities of heat. The refrigerant itself, after the work has been performed upon it and after it has absorbed heat from the substance to be cooled and delivered heat to the environment, is back in the state in which it was at the outset. It has passed through a refrigerating cycle and is now ready to pass through the same cycle again.

When the refrigerating process consists in liquefying a gas it is frequently unnecessary to employ a separate refrigerant. The gas that is to be liquefied can itself serve as the refrigerant or working substance. Thus, in the usual type of liquid-air plant, of which we shall have more to say later, the air itself is the working substance. While part of the air that enters the plant is liquefied, the other part leaves at room-temperature, after having served as a refrigerant to liquefy the first part. When a quantity of air enters a liquefier we cannot state which individual molecules are going to serve as refrigerant and which are destined to be converted into liquid air, although we can compute how much of the ingoing air will actually be liquefied. This state of things makes it rather difficult to understand the working of a gas liquefier.

Since it is not always easy to distinguish between what is cooling and what is being cooled, it is customary to treat these plants as if they were not refrigerators at all, thus completely veiling the real nature of the process. We shall attempt to avoid this mistake and bring out, as far as possible, the characteristic points of refrigeration in the liquefaction and separation of gases.

Suppose that we desire to cool a substance from a temperature T_1, say room-temperature, to a temperature $T_2 < T_1$. To do this we shall have to give off a certain amount of heat $-Q_1$ to the surroundings and a certain amount of work W' will have to be performed. Then

$$W' = \Delta U - Q_1,$$

where ΔU is the increase in internal energy of the substance. Actually ΔU is negative. As in the case treated at the end of the last chapter, part of this work may be done by the atmosphere, and to this we do not have to contribute. The net work will therefore again be

$$W = \Delta U + \Delta pV - Q_1 = \Delta H - Q_1.$$

On the other hand, $$\Delta S \geqslant Q_1/T_1.$$

So we have again, as in the last chapter,

$$W \geqslant \Delta H - T_1 \Delta S.$$

If the process consists in cooling and finally liquefying a gas, the expression

$$W_{\text{rev}} = \Delta H - T_1 \Delta S$$

is called the *reversible work of liquefaction*. It is the minimum work needed to convert the gas into a liquid, starting at room-temperature, and is quite independent of whether a special refrigerant is used or not, depending merely on the enthalpy and entropy of the substance to be cooled. The change of enthalpy ΔH to be brought about is called the required *refrigerating performance*.

At first sight it would appear that a plant for separating a gaseous mixture, in which, as a rule, the mixture enters and the products leave at room-temperature, is not a refrigerator at all. The term ΔH in equation (20) of p. 111 is negligibly small as compared with the other terms; in the case of perfect gases it is indeed zero. Apparently gas separation as such requires no refrigerating performance. However, the presentation given in Chapter IV was not quite accurate. We there assumed that the heat introduced and withdrawn from the system was transferred reversibly. This is not the case in practice. Actually there will always be an irreversible heat transfer from the warm environment to those parts of the plant that are at low temperatures. These heat

leaks can never be eliminated completely and require permanent compensation. It is the compensation of these losses, i.e. the maintenance of the low temperatures in the plant, that requires a constant refrigerating performance in the stationary state, in the same way as this is required of an ordinary refrigerator in the kitchen. This may be expressed very simply by means of a balance equation. Suppose 1 lb. of refrigerant, which may or may not be the gas that is being liquefied, to be circulating through the apparatus in a given time. Let h_1 be its specific enthalpy on entering the plant and h_2 its enthalpy on leaving. And suppose that an amount of heat q leaks into the plant during the same time. Then, in the stationary state, the balance of heat requires that $h_2 - h_1 = q$. The enthalpy of the gas leaving must be greater than that of the gas entering the apparatus and the required refrigerating performance per pound of refrigerant is q.

In practice the gas will leave the plant slightly below room-temperature, owing to imperfect heat exchange. This will also require compensation in the form of additional refrigerating performance.

During the period of cooling, before the stationary state is reached, a gas-separating plant is clearly a refrigerator in the ordinary sense of the word. Usually the refrigerating performance in this period is much greater than in the stationary state.

Finally, it may be expedient to withdraw some of the products of separation in the liquid state, as in the liquid oxygen industry. In this case a very much greater refrigerating performance is required, equal to the difference in enthalpy of gaseous oxygen at room-temperature and atmospheric pressure and liquid oxygen at its boiling-point.

We see that every gas-separating plant requires a certain amount of refrigeration, though the amount will differ appreciably according to the type of plant we have in mind.

In recognizing that refrigeration necessitates the expenditure of work and the delivery of heat to the environment, we have as yet accomplished little. For, of course, not every expenditure of work and delivery of heat will lead to refrigeration. We have still to show how these operations may be so coordinated as to result in the lowering of the temperature of a body and in the withdrawal of heat therefrom.

2. Thermodynamic diagrams

We have seen that separation and refrigeration require a definite expenditure of work, which is a function of the enthalpy and entropy of the substance to be treated. It has been shown that separation can

be suitably represented on a diagram involving enthalpy, entropy, and composition. Refrigerating processes are usually not connected with changes of composition: either the refrigerant is itself a pure substance or, as in the case of air, its composition remains practically unchanged while it is being cooled or liquefied. The diagrams employed in studying refrigerating processes will therefore be able to dispense with concentration as a variable.

The most important variables of refrigerants are pressure, temperature, enthalpy, and entropy. For certain purposes volume is also useful. These properties can be arranged in several diagrams, two variables being taken as ordinates and abscissae, and the lines on the diagrams representing constant values of the other variables. The most frequent diagrams are (h, T), $(\log p, h)$, (T, s), and (h, s). Though all complete diagrams are theoretically equivalent, some are more convenient for some purposes and some for others.

The values of h, s, and v as functions of p and T can be obtained by simple differentiation from the characteristic potential of these two variables, which is the Gibbs potential $g = u - Ts + pv$. For

$$s = -\left(\frac{\partial g}{\partial T}\right)_p, \qquad h = g - T\left(\frac{\partial g}{\partial T}\right)_p, \quad \text{and} \quad v = \left(\frac{\partial g}{\partial p}\right)_T. \tag{1}$$

So, whether or not the Gibbs potential is actually evaluated, the data needed to construct a thermodynamic diagram are the same as those needed to calculate g. Now, apart from arbitrary constants,

$$g(p, T) = \int_{p_0}^{p} v(p, T)\, dp - T \int_{T_0}^{T} \frac{dT}{T^2} \int_{T_0}^{T} c_p(p_0, T)\, dT, \tag{2}$$

where p_0 and T_0 are any chosen pressure and temperature and c_p is the specific heat at constant pressure. The data needed are therefore (1) $v(p, T)$, i.e. an 'equation of state' valid in the whole interval of pressure and temperature with which we are concerned, or (p, v, T) relations equivalent to such an equation of state; (2) c_p as a function of temperature for one arbitrarily chosen pressure.

Now there is no objection to choosing p_0 so low that the vapour may be considered as a perfect gas. Then the calorimetric measurement of c_p can be replaced by a theoretical value, taken from statistical mechanics. The evaluation of g, and therefore of h and s, is thus possible on the basis of accurate (p, v, T) measurements alone. Nor is it necessary to calculate g first in order to obtain h and s. Thus, for a diatomic gas we can assume that $c_p = \frac{7}{2}R$, irrespective of temperature

at $p = 0$.† With the relation

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p \tag{3}$$

we can then calculate c_p for all pressures and temperatures. This enables us to compute h by integrating c_p at constant pressure over the temperature interval required. We can find s from c_p and our (p, v, T) relations by using

$$\left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T} \quad \text{and} \quad \left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p, \tag{4}$$

if v as a function of p and T is assumed to be known.

Generally (p, v, T) data are not known with sufficient accuracy over the whole interval of pressure and temperature, and h as a function of p and T can be determined from the following data:

(1) a single (p, v) isothermal, usually at room-temperature;
(2) the vapour pressure or saturation curve;
(3) the latent heat of evaporation λ as a function of temperature;
(4) one of the following three partial derivatives, determined over a wide field of temperature and pressure:
   (a) the specific heat at constant pressure $c_p = (\partial h/\partial T)_p$;
   (b) the Joule-Thomson coefficient $\mu = (\partial T/\partial p)_h$;
   (c) the isothermal expansion coefficient $\alpha = (\partial h/\partial p)_T$.

Specific heats of gases are not easy to determine accurately and method (a) has not so far been employed. Though the determination of μ is difficult and involves rather complicated apparatus, the method has been very carefully developed and yields accurate results. The work of Hausen‡ and of Roebuck and Osterberg§ has furnished valuable and extensive data on the Joule-Thomson coefficient, so that method (b) is considered the most reliable for evolving thermodynamic diagrams. A method for measuring α was developed some years ago by Eucken, Clusius, and Berger.‖ It was used by them to compile an (h, T) diagram of methane.

Hausen evolved an (h, T) diagram of air from his own measurements of μ as follows. Choosing the arbitrary constant in h so that $h = 50$

† With the exception of hydrogen, the rotational degrees of freedom of diatomic gases are fully excited at the temperatures concerning us. Vibrational degrees of freedom need not be taken into account.

‡ H. Hausen, *Forsch. auf dem Geb. des Ingenieurwesens*, 1924, 274.

§ J. R. Roebuck and H. Osterberg, *Phys. Rev.* **48**, 450 (1935).

‖ A. Eucken, K. Clusius, and W. Berger, *Zeits. f. Kälteindustrie*, **41**, 145 (1935); *Zeits. f. techn. Physik*, **6**, 267 (1932).

cal./gm. at $p = 0$ and $T = 0°$ K., and assuming $c_p = 7R/2M = 0{\cdot}241$ cal./deg. gm. at $p = 0$, where M is the molecular weight of air, he obtains for the line of constant pressure zero on the (h, T) diagram (see Fig. 84)

$$h = 50 + 0{\cdot}241T \text{ cal./gm.}$$

The other lines of constant pressure in the gaseous region are then obtained from the experimental values of μ with the relation

$$T_2 - T_1 = \Delta T = \int_1^2 \mu \, dp. \tag{5}$$

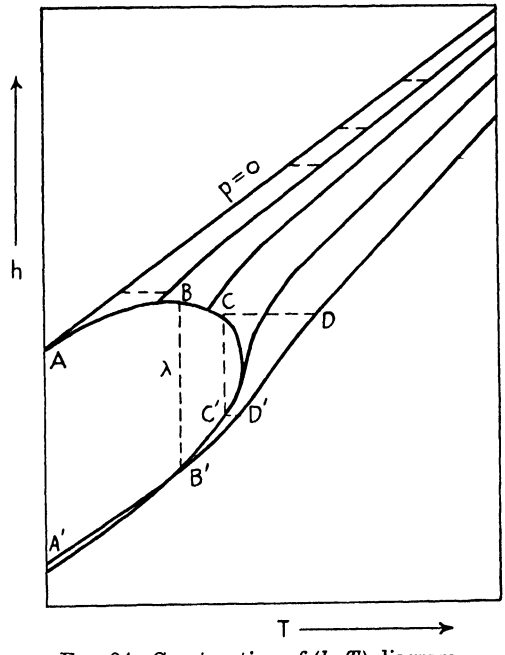


FIG. 84. Construction of (h, T) diagram

The vapour branch of the boundary line from A to point B having a horizontal tangent is obtained in the same way, taking the integral of μ from the saturation temperature to $p = 0$. The liquid branch from A' to B' is then plotted from the known heats of evaporation. Curves of constant pressure to the right of $A'B'$ are constructed by integrating μ from the high-pressure side to the boundary curve. To obtain the part of the boundary curve to the right of BB' we must combine latent heats with integrated values of μ. For a given pressure we know the corresponding temperature on the saturation curve as well as the corresponding value of λ. This gives us two points C and

C', whose distance from each other we know, as well as their distance from the ordinate axis; but we do not yet know their height above the axis of abscissae. We can obtain the length of two lines DC and $D'C'$ by integrating μ from a certain high pressure to the saturation pressure at CC'. We now have a group of four points $DCC'D'$, which we know but for the height of the group as a whole above the axis of abscissae. We can then determine other such groups, which must finally be so arranged that the boundary line, as well as the line of constant pressure on which the D's lie, become smooth curves. This can be done with sufficient accuracy and the (h, T) diagram with lines of constant pressure can thus be completed.

The entropy may then be obtained as follows:

Since
$$ds = c_p\,dT/T - (\partial v/\partial T)_p\,dp, \tag{6}$$
we have for a given temperature
$$s = s_0 - \int (\partial v/\partial T)_p\,dp, \tag{7}$$
where s_0 is an arbitrary constant, which is so chosen that, for $p = 1$ atm., the entropy of liquid air at the boiling-point is zero. For room-temperature the isothermal for air is very accurately known, and so $\int (\partial v/\partial T)_p\,dp$ can be computed accurately for this temperature. Now at constant pressure
$$ds = c_p\,dT/T = dh/T. \tag{8}$$
So, as we know s for all values of p at room-temperature, we can compute it for all other temperatures and pressures from the (h, T) diagram by taking
$$s = s_0 + \int_{T_0}^{T} dh/T. \tag{9}$$
We can now insert the lines of constant entropy in the (h, T) diagram and also construct a (T, s) diagram with lines of constant enthalpy.

Finally, the specific volume v can be computed from μ with the equation
$$\mu = \left(\frac{\partial T}{\partial p}\right)_h = \frac{T(\partial v/\partial T)_p - v}{c_p} = \frac{T^2}{c_p}\left(\frac{\partial (v/T)}{\partial T}\right)_p. \tag{10}$$
For constant pressure this gives
$$d\left(\frac{v}{T}\right) = \frac{\mu c_p}{T^2}\,dT = \frac{\mu}{T^2}\,dh \tag{11}$$
and
$$\frac{v}{T} = \frac{v_0}{T_0} + \int_{T_0}^{T} \frac{\mu}{T^2}\,dh. \tag{12}$$

In this way all the thermodynamic properties can be determined and the diagrams may be constructed. Figs. 85, 86 show the (h, T) and (T, s) diagrams of air, as computed by Hausen on the basis of his experiments. A further set of diagrams for air, based on more recent data, have been constructed in English engineering units by V. C. Williams.†

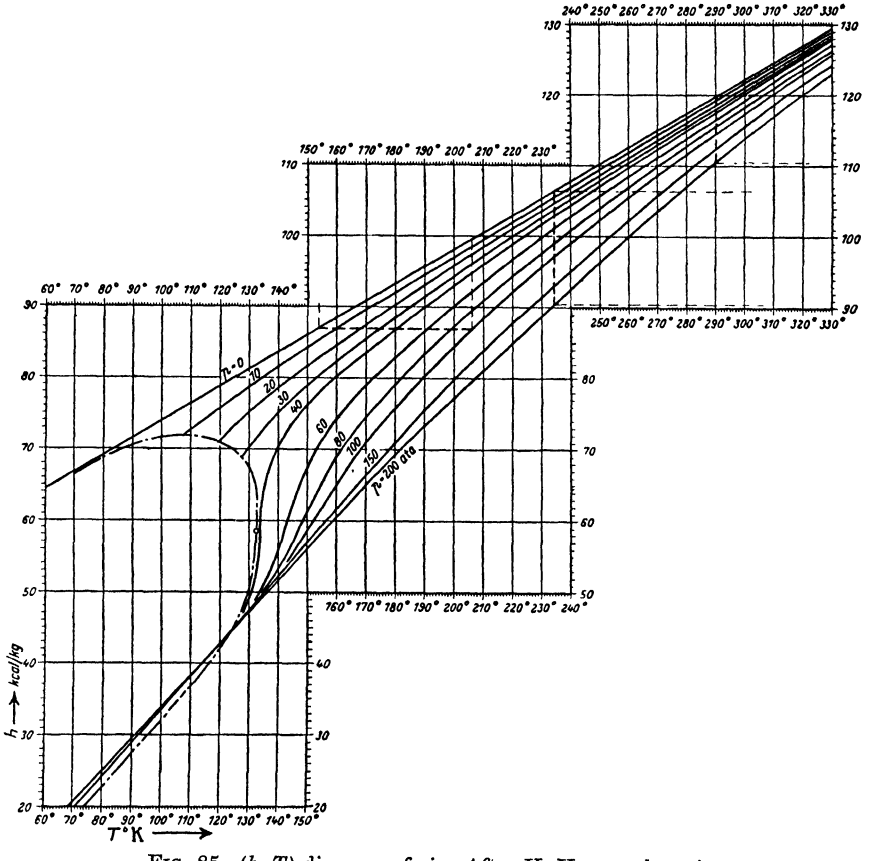


FIG. 85. (h, T) diagram of air. After H. Hausen, loc. cit.

3. Refrigerating cycles

We can now answer the question as to how the performance of work and the delivery of heat may be so coordinated as to produce refrigeration. Suppose that we wish to cool a gas, say air, from room-temperature T_1 to a low temperature T_2. The refrigerant is to be air itself and the pressure is to be atmospheric before and after the operation. From Fig. 86 we see that this requires a decrease in enthalpy and entropy

† V. C. Williams, *Trans. Am. Inst. Chem. Eng.* **39**, No. 1 (1943).

of the air to be cooled, and from p. 113 we know that the work to be done is at least $\Delta H - T_1 \Delta S$.

The only way we can perform work on air is by compressing it. If we do this at constant room-temperature, making use of a heat reservoir at T_1, say water, we shall be delivering heat to this reservoir and

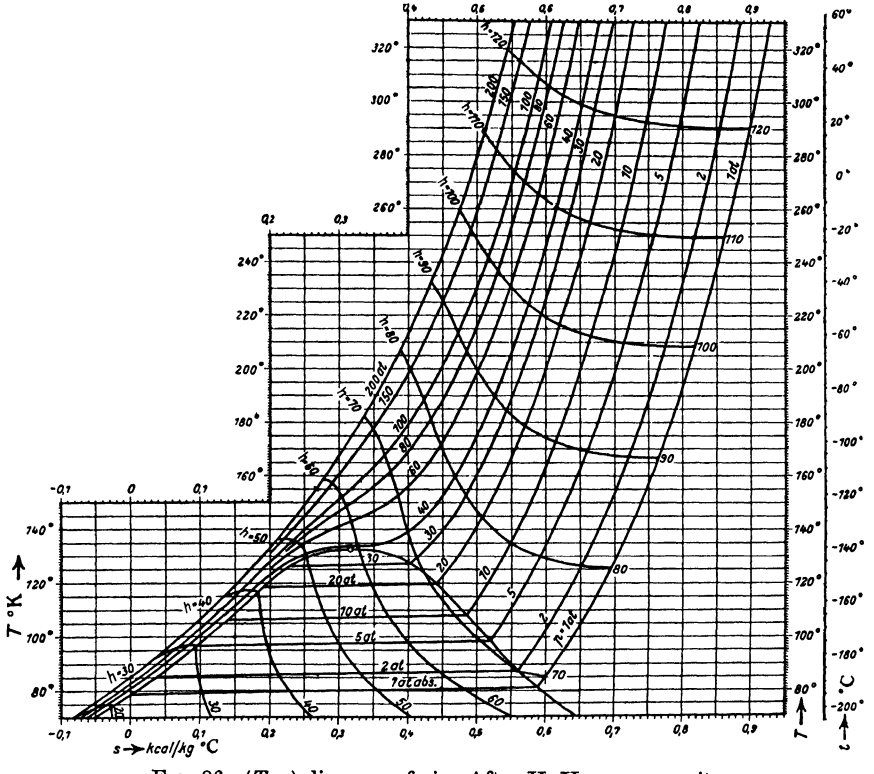


FIG. 86. (T, s) diagram of air. After H. Hausen, op. cit.

simultaneously we shall be decreasing the enthalpy and entropy of the air, as may be inferred from Fig. 87, AB. We can now perform one of the two following operations:

(1) we can expand the air at constant enthalpy along the curve BC;

(2) we can expand it at constant entropy along BD.

The first operation may be carried out by allowing the air to expand in a throttle valve. This is a so-called Joule-Thomson expansion, in which H remains constant. It is characterized by the fact that, all through the expansion, the pressure on the low-pressure side of the valve is always atmospheric and thus much smaller than the momentary pressure on the high-pressure side, except right at the end of the

expansion. The process is therefore irreversible, and the entropy increases. However, as Fig. 87 shows, the increase in entropy during the expansion is less than the decrease during the compression, so that finally the entropy of the air is less than at the commencement of the cycle. Since the enthalpy remains constant during the expansion, the total decrease in enthalpy is equal to that incurred during the compression. The air has passed through a refrigerating cycle, as a

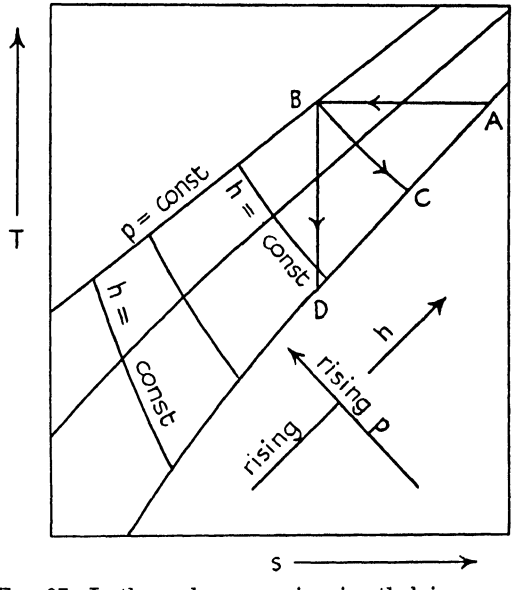


FIG. 87. Isothermal compression, isenthalpic expansion, and isentropic expansion on (T, s) diagram

result of which its temperature, enthalpy, and entropy have been reduced. This cycle is called a *Linde* cycle, after Carl von Linde, who first used it to liquefy air in 1895. Strictly speaking, the cycle is, of course, incomplete, as the air, in its capacity of refrigerant, is not in the same state afterwards as beforehand. This is because the same air, in its capacity of the object of refrigeration, has been cooled. This apparent confusion will be removed presently, when we shall see how the cycle is completed.

If the expanding air is made to move the piston of a reciprocating engine or the rotor of a turbine in such a way that the pressure it is operating against is always the same as, or very slightly less than, its own momentary pressure, the process is practically reversible, and so the entropy of the air will remain very nearly constant. On Fig. 87

the air will therefore move along the vertical line *BD*. In this case the entire reduction of entropy undergone by the air during compression will be maintained during the expansion, and, as we see from Fig. 87, the temperature and enthalpy will be reduced further than in the Linde cycle. This is known as the *Claude* cycle; it was first employed by Georges Claude to liquefy air in 1902. We see that the Claude cycle is apparently more potent than the Linde cycle, as its refrigerating performance is greater.

The Linde and Claude cycles were conceived in order to liquefy air with a view to its subsequent separation into oxygen and nitrogen. Neither of the operations described is in itself sufficient to cool the air to its point of condensation, still less to bring it into the liquid state. To do this, the process must be repeated in such a way that its refrigerating performance will be cumulative. This is effected with the help of a heat-exchanger. The introduction of the heat-exchanger is of vital importance in gas liquefaction; it is indeed the exchanger that makes the liquefier a refrigerator. When after expansion in the valve or cylinder the cold gas returns through the heat-exchanger, it is made to precool incoming warm gas. Here it plays the part of a refrigerant, in that it absorbs heat from the warm air. The transfer of heat takes place throughout the whole length of the heat-exchanger, out of which the expanded air emerges practically at room-temperature. In this way the entire refrigerating performance of the cycle remains inside the plant, the gas reappearing in the same state as it was in before compression. Only now is the cycle complete. The result is that the compressed air now reaches the valve or the cylinder at a lower temperature than before and, after expansion, its temperature is still lower. The temperature in front of and behind the valve or cylinder continues to fall until part of the air is liquefied in the course of the expansion.† The liquefied air collects at the bottom of the apparatus and thereafter ceases to take part in the process; more especially, it no longer serves as a refrigerant. As the liquefied portion of the expanded air increases, the amount of refrigerant at our disposal decreases, until the refrigerating performance is no longer sufficient to lower the temperature any further. A stationary state is thus brought about, in which a certain fraction ϵ of the incoming air is liquefied, the remainder $(1-\epsilon)$ acting as refrigerant. After the stationary state has been attained the quantity and state of the air at all points of the plant remain the same and no

† In the Claude process liquefaction does not actually take place in the cylinder, but in an auxiliary cycle to be described later.

longer depend on time, except in so far as liquid air is allowed to accumulate in the receiver.

During the stationary state of an air-liquefier a certain fraction $(1-\epsilon)$ of the incoming air serves as a refrigerant, its function being to cool and liquefy the rest of the air. Before the stationary state is reached, all the air can be considered as refrigerant and its function is to cool itself. But since heat is nowhere withdrawn from the plant at a low temperature before the liquid is formed and drawn off, the refrigeration during the preliminary period is not apparent. It consists merely in lowering the temperature of the air in certain parts of the plant and of the metal tubes and vessels of which it is built. In the preliminary period we may say with equal justification that the air is cooling and that it is being cooled.

4. The air-liquefiers of Linde, Claude, and Heylandt

Linde and Claude are not the first pioneers of gas liquefaction. In 1877, eighteen years before Linde invented his cycle, small quantities of liquid oxygen were produced by Louis Cailletet in France and by Raoult Pictet in Switzerland. In the eighties all the then known permanent gases except hydrogen were liquefied regularly in Olszewski's laboratory at Cracow and the properties of the liquids were studied. In the early nineties Dewar was experimenting with liquid air in England and Kamerlingh Onnes was building his famous low-temperature laboratory at Leiden in Holland. Onnes's air-liquefier, which was based on the cascade principle, of which we shall have more to say later, was set up in 1892.

The great achievement of Linde is that he was the first to conceive the industrial implications of gas liquefaction and to put these ideas into practice. Linde realized that, through the liquefaction of gases, it would be possible to apply the well-known fractionating methods of the alcohol industry to the separation of air, and so to produce cheap oxygen. He foresaw that the production of liquid air on a commercial scale would be a profitable undertaking and would lead to the development of a new industry. Linde's apparatus was the first continuously operating machine, the first 'cycle', in the full sense of the word, for liquefying gases. Industrial gas-liquefaction, and, in consequence, industrial gas-separation, undoubtedly date from Linde's invention.

Several processes, the most famous of which were the Claude and Heylandt cycles, were developed shortly after the Linde liquefier appeared on the scene. All were subsequently combined with various

separating units, for which they supplied the necessary refrigeration. In this section we shall consider air-liquefiers as such, distinct from their ulterior object of leading to the separation of air into its components.

In comparing various types of liquefier, it is best to determine the work required in each case to produce a certain quantity—say 1 gallon —of liquid air. This will give us a measure for the efficiency of a liquefier.

We shall find that, in every case, the work consists in compressing the air and, occasionally, some auxiliary gas, to a definite pressure. Moreover, in every liquefier only a part of the compressed air is actually liquefied, the rest returning through heat-exchangers and acting as a refrigerant. The fraction that is liquefied is known as the *coefficient of liquefaction* and denoted by ϵ. Evidently, the greater ϵ, the more efficient will be the liquefier, other things being equal. For to produce 1 gallon of liquid air, we must compress a quantity of air equivalent to 1 gallon of liquid divided by ϵ. If ϵ is very small, we must compress large quantities of air in order to obtain 1 gallon of liquid.

The work required to compress isothermally 1 mole of a perfect gas from a pressure p_2 to a pressure p_1 is equal to $RT\log(p_1/p_2)$, where R is the gas constant and T the absolute temperature. For air at room-temperature this expression is tolerably accurate up to moderately high pressures. The correct thermodynamic formula for the work required in compressing real gases is

$$W = \Delta H - T_0 \Delta S, \tag{13}$$

where ΔH and ΔS are the changes in enthalpy and entropy respectively incurred when the gas is compressed isothermally from p_2 to p_1 at a temperature T_0. Since thermodynamic diagrams have been constructed for air and for a number of other gases there is no difficulty in applying this formula.

There are two ways of defining the work needed to produce a gallon of liquid air with an apparatus of a given type. One is the work needed in theory on the assumptions that the compression is really isothermal and that there are no thermal and frictional losses. The other is the work actually needed in practice. Usually the latter is about twice as great as the former. To allow for frictional losses in the compressor and for the fact that the compression is never really isothermal but made up of a number of almost adiabatic stages, it is customary to multiply the theoretical work of compression by a factor of about 1·7. This figure is not very accurate as it will depend to a considerable

extent on what type of compressor is used and especially on the number of stages. The thermal losses in the liquefier itself are caused by heat leakage through the lagging and by temperature heads at the warm ends of heat-exchangers, the expanding gases leaving the exchangers at a temperature lower than that of the environment. In well-constructed plants these temperature heads are usually about 3° C.; when cold accumulators are used instead of exchangers they can be brought below 2° C. Heat leakage through the lagging is very serious in small liquefiers but far less important in large plants. In large-scale industrial apparatus it is roughly 0·3 B.Th.U. per cubic foot of gas (about 2½ kcal./cub. m.).

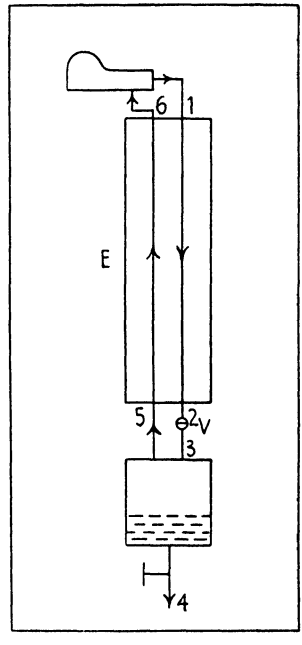


FIG. 88. Simple Linde liquefier

For calculations in this section we shall keep to the theoretical work of liquefaction, mentioning practical figures only occasionally for comparison. It should be pointed out that the theoretical work of liquefaction is quite distinct from the reversible work of liquefaction mentioned on p. 113. Whereas the latter is the minimum work needed in theory to produce a gallon of liquid air, using a fictitious reversible liquefier, i.e. the most efficient type of liquefier imaginable, the theoretical work of liquefaction is based on a certain type of liquefier, which in general involves irreversible processes, and merely assumes that this particular plant is perfectly lagged, cooled, and lubricated.

Linde liquefiers. We have already stated that the Linde liquefier is based on the isenthalpic expansion of compressed air. In its simplest form the plant consists of a compressor, a heat-exchanger, an expansion valve, and a vessel to collect the liquid. The liquefier is shown schematically in Fig. 88. Compressed air enters the heat-exchanger E at 1 and leaves it at 2. It is thereupon expanded in the valve V, so that, in the stationary state, it is partly liquid at 3. The liquid is drawn off at 4; the remaining vapour re-enters the heat-exchanger at 5 and finally leaves it at 6, after being warmed to almost room-temperature and so precooling the incoming compressed air. The process is illustrated on the (T, s) diagram in Fig. 89.

To determine the coefficient of liquefaction ϵ, consider the heat

balance of the whole plant behind the compressor in the stationary state. Suppose a certain quantity of air is introduced at 1 in a certain period of time. Then $H_1 = \epsilon H_4 + (1-\epsilon)H_6$,

so that
$$\epsilon = \frac{H_6 - H_1}{H_6 - H_4} = \frac{h_6 - h_1}{h_6 - h_4}. \tag{14}$$

Now h_4 and h_6 are the specific enthalpy of air as a saturated liquid and at room-temperature respectively, both at atmospheric pressure, and

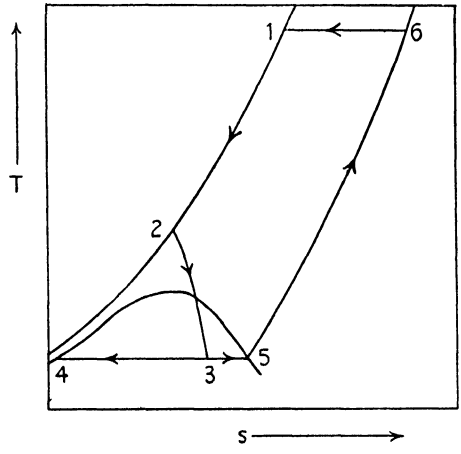


FIG. 89. Simple Linde cycle on (T, s) diagram

are thus material constants of air and independent of the nature of the plant. The only variable in the expression for ϵ is h_1, which, at room-temperature, is a function of the pressure alone. Thus ϵ depends merely on the pressure to which the air is compressed.

In order to liquefy 1 kg. of air, we must reduce its enthalpy from h_6 to h_4. $h_6 - h_4 = q$ is therefore the refrigerating performance required, and we can write
$$\epsilon q = h_6 - h_1. \tag{15}$$

On the other hand, liquefaction of 1 kg. requires that $1/\epsilon$ kg. be sent through the plant. The refrigerating performance of $1/\epsilon$ kg. is therefore q, and that of 1 kg. is $\epsilon q = h_6 - h_1 = q'$.

The work required may be computed from
$$W' = \Delta H' - T_0 \Delta S', \tag{16}$$

where $\Delta H'$ and $\Delta S'$ give the increase in enthalpy and entropy resulting from the compression of air from atmospheric pressure to the pressure used in liquefaction. Both quantities are negative. Using Hausen's

(T, s) and (h, T) diagrams for air, in which h is given in kcal./kg. and s in kcal./kg. deg. C., we obtain the following data for working pressures of 50, 100, and 200 atm.

TABLE 12. *Simple Linde Liquefier*

$h_4 = 22, \quad h_6 = 121, \quad s_6 = 0{\cdot}893$

p_1	*50*	*100*	*200 atm.*
h_1	117·5	114·8	111·1 kcal./kg.
s_1	0·630	0·580	0·518 kcal./kg. deg. C.
ϵ	0·034	0·063	0·100
w'	0·0856	0·0983	0·116 kcal./kg. of compressed air
$w = w'/\epsilon$	2·52	1·56	1·16 kWh/kg. of liquid air
w	9·98	6·18	4·59 kWh/gallon of liquid air

We can evaluate the reversible work of liquefaction from

$$W_{\text{rev}} = \Delta H - T_0 \Delta S, \tag{17}$$

where ΔH and ΔS denote the difference between the enthalpy and entropy of liquid air boiling under atmospheric pressure and gaseous air at room-temperature and atmospheric pressure. With Hausen's data this gives

$$w_{\text{rev}} = 0{\cdot}73 \text{ kWh/gallon of liquid air.}$$

If we take w_{rev}/w as a measure of the efficiency of the liquefier, we find that even the theoretical efficiency of a simple Linde liquefier, working at the relatively high pressure of 200 atm., is only 16 per cent. In practice the efficiency is not more than 8 per cent.

There are two ways of raising the efficiency of Linde liquefiers, both of which have been successfully applied. We may either seek to lower the work of compressing a given quantity of air, or we may try to raise the coefficient of liquefaction. At first sight the first suggestion may seem absurd, for it would apparently necessitate lowering the working pressure, and we have already seen that this leads to so great a decrease in ϵ as far to outweigh the reduction in the work of compression. But there is another way of reducing this work: instead of lowering the high pressure, we can raise the low pressure. The liquefied air itself must, of course, be expanded to 1 atm., as it could not otherwise be tapped off, but we have seen that ϵ is only a small fraction of the amount of air compressed. There is no necessity to expand the rest of the air to 1 atm. If we expand it to an intermediate pressure of some 40 atm., the refrigerating performance will be but slightly reduced, while the work of compression will be very much smaller. For it will mean that the greater part of the air passing through the plant will circulate merely between

40 and 200 atm. instead of between 1 and 200 atm. Since the work of compression is roughly proportional to $\log(p_1/p_2)$, compression from 40 to 200 atm. costs much less than compression from 1 to 40 atm. From our preceding discussion it is evident that this so-called *Linde high-*

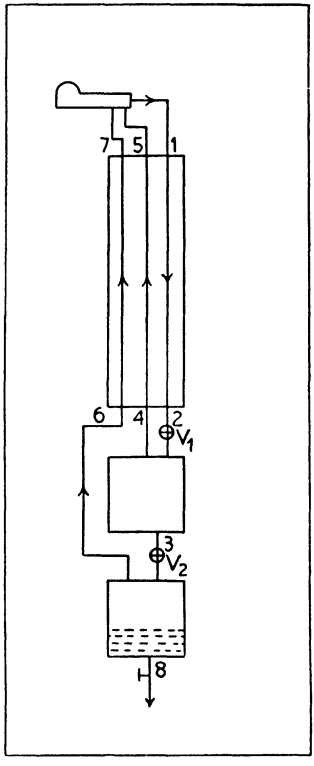


FIG. 90. Linde high-pressure cycle

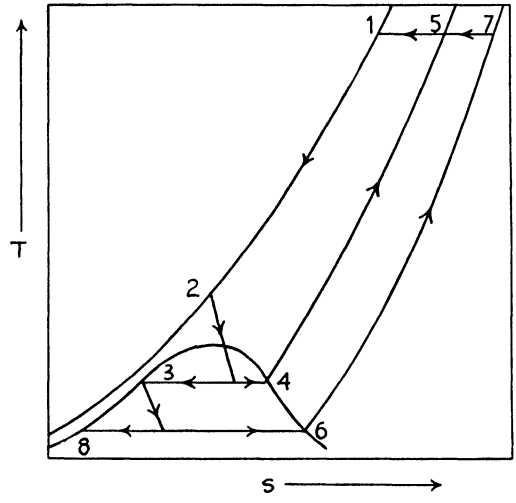


FIG. 91. Linde high-pressure cycle on (T, s) diagram. This diagram holds when the intermediate pressure is below the critical pressure of air (38·4 atm.). Otherwise points 3 and 4 coincide in a point outside the inhomogeneous region

pressure cycle is characterized by a stronger differentiation between cooled air and cooling air than is the case in the simple liquefier. While the liquefied air is emitted at atmospheric pressure, most of the refrigerant is made to operate between a high pressure of 200 atm. and an intermediate pressure of about 40 atm.

The Linde high-pressure cycle is shown schematically in Fig. 90 and in diagram in Fig. 91. In the valve V_1 the compressed air leaving the heat-exchanger is expanded to the intermediate pressure, and in V_2 a certain portion μ is further expanded to 1 atm., part being liquefied.

$(1-\mu)$ passes back through the exchanger at intermediate pressure via 4–5 and is readmitted to the highest stage of the compressor. The low-pressure side of the compressor takes in only as much air as is actually liquefied plus what emerges at 7.

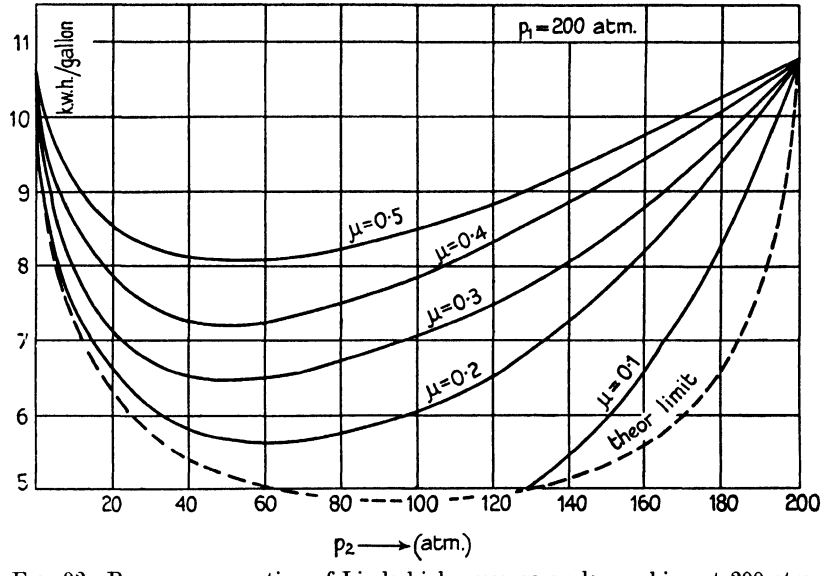


FIG. 92. Power consumption of Linde high-pressure cycle, working at 200 atm. high pressure, as a function of intermediate pressure for various amounts of gas expanded to 1 atm.

The balance equation now reads

$$h_1 = (1-\mu)h_5+(\mu-\epsilon)h_7+\epsilon h_8,$$

which gives

$$\epsilon = \frac{h_5-h_1+\mu(h_7-h_5)}{h_7-h_8}. \qquad (18)$$

The coefficient of liquefaction here depends not merely on the working pressure p_1 but also on the intermediate pressure p_2 and on the amount of air μ expanded to 1 atm. The work needed also depends on these three independent variables. The calculations can again be made with the help of Hausen's diagrams. Fig. 92 shows the amount of work needed *in practice* to produce a gallon of liquid air by this method with a working high pressure of 200 atm., as a function of the intermediate pressure p_2, for various values of μ. The Linde plants usually work at $\mu \sim 0{\cdot}2$ and p_2 from 40 to 50 atm. In this case $\epsilon = 0{\cdot}08$, i.e. rather less than in the case of the simple liquefier, but the work of liquefaction is reduced to 3·23 kWh/gal. theoretically and about 6·0 kWh/gal. in practice.

The dotted line in Fig. 92 marks the limits up to which the high-pressure cycle can be applied. The existence of such limits can be inferred as follows. The Linde method is based on the fact that isenthalpic expansion of air leads to a fall in temperature, i.e. that the Joule-Thomson coefficient $(\partial T/\partial p)_H > 0$. It is as a result of this that the low temperature needed for liquefaction is actually attained. Later, in the stationary state, actual liquefaction, as we have seen, depends on the enthalpy difference between compressed and expanded air at room-temperature, i.e. on $\int_{p_2}^{p_1} (\partial H/\partial p)_T \, dp$, but it is the positive sign of $(\partial T/\partial p)_H$ that enables us to reach the low temperature and so to set up the stationary state to begin with. That is to say, that only such final states can be attained by the Linde method as can be reached from room-temperature through a complete series of intermediate states in which $(\partial T/\partial p)_H > 0$. Now at low temperatures and high pressures $(\partial T/\partial p)_H$ becomes negative. This may be seen from Fig. 85, in which the lines of constant pressure intersect near the saturation curve at the bottom right-hand side of the figure. It is brought out more clearly in Fig. 93, which shows an exaggerated picture of the (h, T) diagram of air. The essential features are those of Fig. 85, but somewhat caricatured. We see that the point B in the upper part of the figure can be reached from A by means of isenthalpic expansion, starting at a higher temperature. But if we wanted to reach the point B' as a result of isenthalpic expansion, we should have to start from A', which is at a lower temperature than B', since in this region $(\partial T/\partial p)_H$ is negative. And since, in the Linde method, the lowest momentary temperature in the apparatus has always been reached by isenthalpic expansion from a higher temperature, we may infer that the point B' is unattainable. Now if we compute the temperature that must

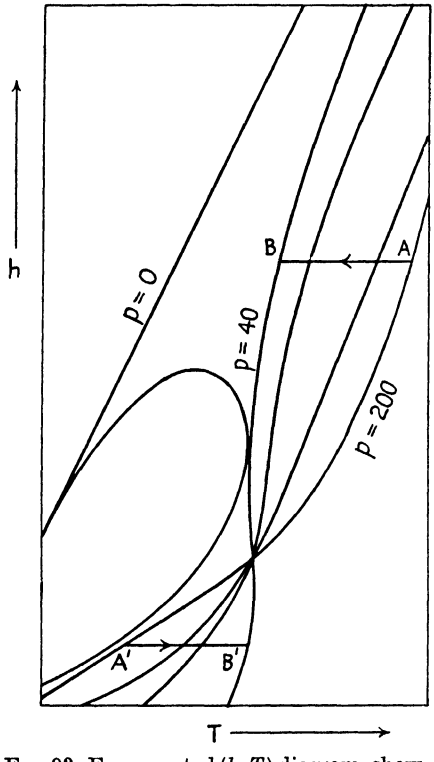


FIG. 93. Exaggerated (h, T) diagram, showing significance of limiting curve in Fig. 92

exist in the intermediate vessel in Fig. 90 in the stationary state, as a function of p_2 and μ, we find that, at points below the dotted curve in Fig. 92, the temperatures and pressures at this point of the plant would be unattainable. In order to obtain a stationary state compatible with the balance equations, we must therefore keep within the region marked by the dotted line.

We have seen that there is, in principle, yet another method of raising the efficiency of the Linde liquefier, which consists in increasing the coefficient of liquefaction ϵ. To achieve this, we must somehow raise the refrigerating performance of the cycle. A hint as to how this may be done can be obtained from studying the (T, s) diagram in Fig. 86. We see that the lines of constant enthalpy become steeper as the temperature falls. That is to say, that isothermal compression leads to a greater decrease in enthalpy, the lower the temperature. Now we can hardly compress air at a low temperature, but we can, quite easily and cheaply, precool the compressed air and so attain the same result. In the *Linde liquefier with auxiliary ammonia cycle* the compressed air is precooled to about $-45°$ C. with liquid ammonia, boiling at reduced pressure. The ammonia refrigerator itself has a high refrigerating performance at this temperature. Thus the increase in ϵ which it brings about outweighs the increased work of liquefaction due to the ammonia refrigerator, so that the total effect of the ammonia cycle is to reduce the amount of work needed to produce a gallon of liquid air. The ammonia cycle can be used with or without the high-pressure cycle. The lowest figure obtained for the theoretical work of liquefaction is *1·91 kWh per gallon.*

Comparative figures for the various types of Linde liquefiers are shown in Table 13.

TABLE 13. *Comparison of Linde Liquefiers*

	Reversible process	*Simple Linde*	*Linde with high pressure*	*Linde with ammonia cycle*	*Linde with high pressure and ammonia*
ϵ	1·0	0·10	0·08	0·21	0·17
w_{theor} (kWh/gallon)	0·73	4·59	3·23	..	1·91
w_{pract} (kWh/gallon)	..	10·3	6·0	5·4	3·5

Claude liquefiers. The essential feature of the second type of air-liquefier, which is associated with the name of Claude, is the more or less isentropic expansion of compressed air in the cylinder of a reciprocating engine. For some duties these engines can be replaced

by turbines.† In no case, however, has a liquefier been based on this principle alone. Claude realized, as a result of his first experiments, that liquefaction in the cylinder itself is very inexpedient and, indeed, hardly possible. Not only is adiabatic expansion in itself very inefficient at temperatures and pressures near the critical point, but immense difficulties are encountered in lubricating the expansion engine at temperatures at which all known lubricants are solid bodies. After an ingenious attempt to lubricate the cylinder with liquid air, Claude resorted to a compromise, in which the expanded air in the cylinder is used to precool a separate cycle of air, the latter being thereupon expanded in a reducing valve and partially liquefied according to the Linde principle.

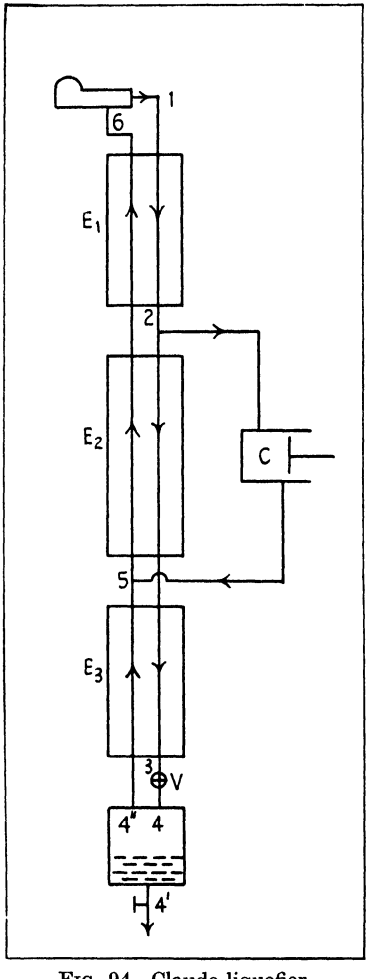


FIG. 94. Claude liquefier

The plant is sketched in Fig. 94 and shown on the (T, s) diagram in Fig. 95. After passing through the first heat-exchanger, E_1, the compressed air separates. One part traverses the other two exchangers, E_2 and E_3, is expanded in the valve V, and partially liquefied. The cold vapour returns through all three exchangers. The rest of the air (the refrigerant proper) is expanded in the engine C and joins the returning low-pressure air at 5. Since the expansion in the engine is never truly isentropic, the line 2–5 in Fig. 95 has been drawn slightly curved. Theoretically it should, of course, be a vertical straight line.

The liquefaction coefficient and power consumption of the Claude plant is a complicated function of a number of parameters: the initial pressure p_1, the fraction μ of air passing through the valve, and the temperature T_2 at which the rest of the air enters the engine. The deviation of the expansion in the cylinder from the isentropic line, and hence the temperature at which it leaves the expansion engine, is itself

† See P. Kapitza, *Journal of Physics, U.S.S.R.* **1**, 7, 1939.

a function of the inlet temperature, as well as depending on the construction of the engine itself. There is little point in computing a theoretical power consumption and we must hence rely on experimental figures.

It has been found empirically that, for each value of p_1 and μ, a definite temperature T_2 exists which renders the power consumption a minimum. If we assume that, in every case, T_2 is so chosen as to comply with this condition, we can plot the empirically determined power con-

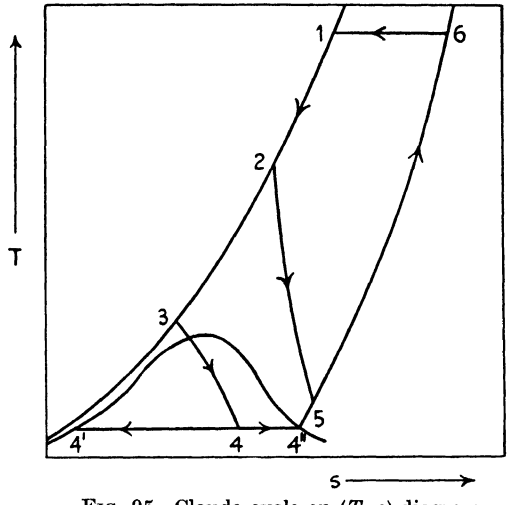


FIG. 95. Claude cycle on (T, s) diagram

sumption as a function of μ for various values of p_1. This has been done in Fig. 96. We see that each curve has a minimum at a certain value of μ, but that this μ increases and the height of the minimum decreases with rising pressure.

The conditions singled out by Claude correspond to the minimum of the curve for 40 atm. About 20 per cent. of the air is expanded in the valve and 80 per cent. passes through the engine. The most advantageous temperature at the intake is $-80°$ C., and this condition is actually realized in Claude's liquefier, the power consumption of which is about *3·6 kWh per gallon* and thus almost exactly the same as in the case of the Linde liquefier with high-pressure and ammonia cycles.

The power consumption at the minimum of the curve marked 200 atm. is *3·2 kWh per gallon*, and the most economical intake temperature in this case has been found to be room-temperature. These are the conditions of the *Heylandt* liquefier, which is now very frequently employed. It is the most efficient plant of this type; for by raising the pressure

above 200 atm. we should simultaneously raise the most profitable intake temperature above that of the environment—a condition which would be hard to fulfil. The Heylandt liquefier has the advantage that it entails no difficulties in lubricating the engine. The air enters at room-temperature and leaves at about —125° C., at which light lubricants such as petroleum ether are quite satisfactory. The apparatus is

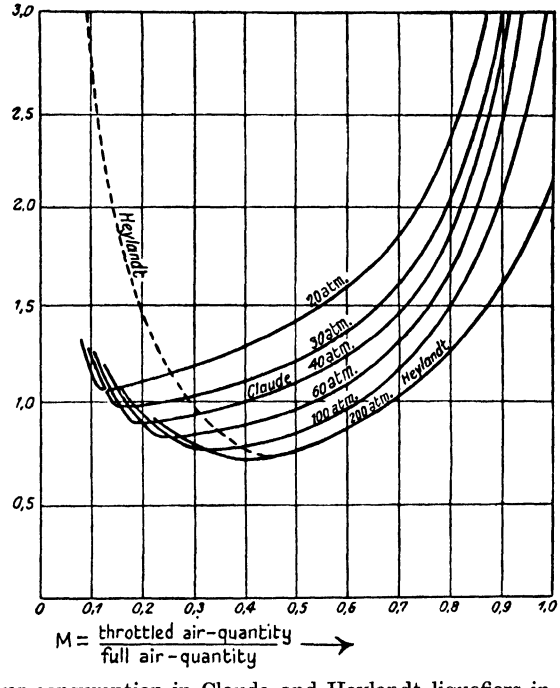


FIG. 96. Power consumption in Claude and Heylandt liquefiers in kWh/kg. as a function of amount of air expanded in valve for various working pressures (1 gallon of liquid air weighs 4 kg.). After W. Lenz, *Handb. d. exp. Phys.* 9 (1929)

further simplified in that the first heat-exchanger in Fig. 94 can be discarded.

In the Heylandt liquefier about 45 per cent. of the air is expanded in the valve and 55 per cent. passes through the expansion engine. Thus, whereas in the Claude plant the valve is a subsidiary appliance and the weight of the process is borne by the expansion engine, the weight of the Heylandt process is fairly evenly distributed between the two. The Heylandt plant, with its comparatively low power consumption, is a very clever synthesis of the principles of Claude and Linde.

The work performed by the air in the expansion engine can be utilized to lower the power consumption. The expansion engine is

generally coupled with the compressor in such a way that the engine 'helps' the compressing motor. Though this help is not very considerable, it is by no means negligible. In the figures given above, this power economy has been taken into account.

In recent years air-expansion turbines have been used to an increasing extent to supply refrigeration for the separation of air. Especially when the pressure differential is low they can now be designed with a high efficiency, although the refrigerating performance is smaller than when a large pressure drop is available. These turbines will be discussed in Chapter VII in connexion with the air-separating plants of which they form a part.

5. The cascade principle and the analysis of losses

We have seen that the minimum amount of work needed to liquefy a quantity of gas is the so-called reversible work of liquefaction

$$W_{\text{rev}} = \Delta H - T_0 \Delta S,$$

which is, of course, merely a function of the properties of the gas to be liquefied and independent of how the refrigeration is carried out. To bring about the necessary reduction in the enthalpy and entropy of air, we employ a refrigerant, which may or may not be air itself, and on which a certain amount of work W is performed. As we have seen, W is always considerably greater than W_{rev}. Now if W_{rev} is sufficient in theory to produce a given quantity of liquid air, how does it come about that an amount of work equal to W_{rev} does not, in practice, produce the effect that it should? The reason can only be that the refrigerating cycle is not a reversible process. For W_{rev} must be independent of how the work is applied, as long as it is reversible. Therefore the question whether a certain type of liquefier is more or less efficient than another reduces to the question whether it is less or more irreversible. Again, as in the preceding chapter, we need a measure of irreversibility.

We already know that this measure is to be found in the changes of entropy undergone within the plant in the stationary state. If we take an entropy balance of the plant as a whole, we find that the sum of the entropies of all substances emerging is always greater than that of all substances entering. The difference of these two sums is a direct measure of the irreversibility of the process. Moreover, the total increase in entropy of the plant as a whole is equal to the sum of the entropy increments incurred in all its individual parts. We can thus

find out what role a given operation, conducted within the plant, is playing in increasing the entropy and thus in increasing W. As we saw in our discussion of separation processes, every increase in entropy ΔS necessitates the expenditure of work to the amount of $T_0 \Delta S$ in addition of W_{rev}, where T_0 is room-temperature, i.e. the temperature at which the work must be performed.

Now in every refrigerating cycle a certain irreversible increase of entropy occurs and this must be compensated by additional work. But the only way this work can be performed is by passing more refrigerant through the plant. This entails a further increase in entropy, since the cycle is irreversible, and for this compensation must again be made, and so on. Thus, if every pound of refrigerant passed through the plant and involving an expenditure of work w^* is accompanied by an irreversible increase of entropy Δs^*_{irr}, only the amount $w^* - T_0 \Delta s^*_{irr} = w^*_{rev}$ is really useful work. If m pounds of refrigerant would be needed to produce a gallon of liquid air in a reversible process, involving the expenditure of an amount of work W_{rev}, then

$$W_{rev} = m w^*_{rev}. \tag{19}$$

But in order to produce the gallon of air with m pounds of refrigerant in our irreversible process, we should have to perform more work on that refrigerant, and the total amount of work performed would be

$$W = mw^* = m(w^*_{rev} + T_0 \Delta s^*_{irr}) = m(w^*_{rev} + w^*_{irr}). \tag{20}$$

Now, instead of performing more work on the refrigerant, we want to pass more refrigerant through the plant, so that the work done on each pound of refrigerant is still w^*_{rev}. Then the amount M of refrigerant needed is given by the relation

$$M w^*_{rev} = m(w^*_{rev} + w^*_{irr}).$$

Hence

$$M = m(1 + w^*_{irr}/w^*_{rev}). \tag{21}$$

To find out what type of liquefier is the most efficient we must first know where entropy changes are likely to occur in liquefiers. We shall here neglect the entropy increases in compressors and confine ourselves to the low-temperature plant itself.

Irreversible changes will occur wherever gases having different temperatures are brought into thermal contact, i.e. in all heat-exchangers and in evaporators and condensers. For there must always be a temperature head where heat is transferred. These sources of entropy increase are generally small compared with those occurring in throttle

valves. We have already shown that this form of expansion is irreversible and it will become apparent that the irreversibility is indeed very serious. But we must now show that the irreversible entropy changes incurred during isenthalpic expansion vary greatly according to the temperature at which the air is expanded. Let us take the expansion of air from 200 to 1 atm., starting at various temperatures. The accompanying entropy increments are shown in the following table:

TABLE 14. *Increase in Entropy in kcal./kg. degree C. during the Isenthalpic Expansion of Air from* 200 *atm. to* 1 *atm.*

T (° *abs.*)	s_{200}	s_1	Δs
320	0·54	0·90	0·36
260	$0{\cdot}47_5$	0·82	$0{\cdot}34_5$
205	0·39	0·69	0·30
160	0·28	0·48	0·20
115	0·14	$0{\cdot}22_5$	$0{\cdot}08_5$

The first three expansions take place wholly in the gaseous phase, the fourth leads to partial liquefaction, the fifth is the expansion of a supercooled liquid leading to partial evaporation. Clearly Δs decreases as the initial temperature falls, and the farther we proceed into the liquid phase the smaller Δs becomes. The isenthalpic expansion of a liquid is far less irreversible than that of a gas.

This fact is very important as it shows us what line to take in order to raise the efficiency of liquefiers. For one thing it explains the advantage obtained from the ammonia cycle. The introduction of the ammonia refrigerant reduces the necessary quantity of refrigerating air, thus lowering the temperature in front of the expansion valve, decreasing the entropy change during expansion, and increasing the coefficient of liquefaction. In the ammonia refrigerator itself the entropy increments are small, since the ammonia is expanded as a liquid. The irreversibility of the plant as a whole is therefore less than in the case of the simple Linde cycle, and so the power consumption is smaller.

But the principle we have just discussed enables us to go much farther in improving the efficiency of liquefiers. Recognizing that expansion of a liquid is more economical than expansion of a gas, we may construct a liquefier in which only liquids are expanded. Air itself cannot be liquefied in liquid ammonia, even if the latter boils at a low pressure. But we can find a series of gases, with progressively falling

boiling-points, each of which may be liquefied under pressure in the condensed phase of the one before it. This is the well-known *cascade principle*, first conceived by Pictet and later carried out by Kamerlingh Onnes and treated theoretically by Keesom.

Keesom's† proposed cascade for liquefying nitrogen contains four cycles: ammonia, ethylene, methane, and nitrogen. The ammonia is

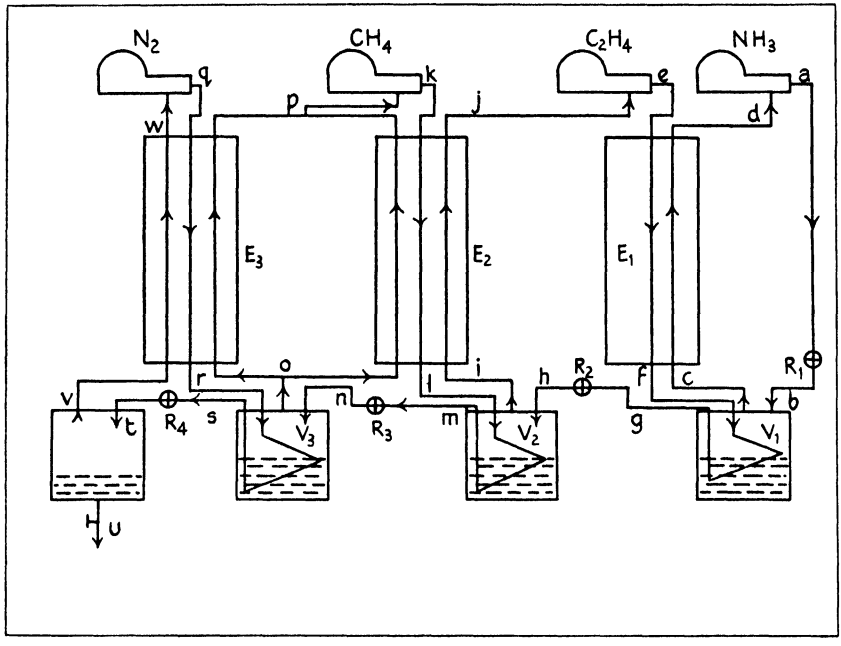


FIG. 97. Keesom's Nitrogen Cascade

liquefied at room-temperature and 10 atm. pressure and the liquid expanded. Ethylene is liquefied at 19 atm. in liquid ammonia, methane at 25 atm. in liquid ethylene, boiling at atmospheric pressure, and finally nitrogen is liquefied in liquid methane at 18·6 atm. This rather complicated apparatus is shown schematically in Fig. 97. It is characterized by the fact that only liquids are expanded. According to Keesom's calculations, the efficiency of this plant should be much greater than that of any of those hitherto described. Including all probable losses, Keesom computes a 'practical' power consumption of only *2·04 kWh per gallon* of liquid nitrogen. The results of Keesom's calculation are set forth in Tables 15 and 16. Table 17 shows the irreversible entropy increments in the various units of the plant.

† W. H. Keesom, *Leiden Commn.*, Suppl. No. 76 *a*.

TABLE 15. *Keesom's Nitrogen Cascade*

m (*kg.*)	*No.*	*p* (*atm.*)	*T* (°*C.*)	*f* †	*h* (*kcal./kg.*)	*s* (*kcal./kg.* °*C.*)
NH_3 0·331	a	10·2	25	..	128·0	1·097
	b	1·0	−34	0·196	128·0	1·128
	c	1·0	−34	1·000	390·8	2·224
	d	1·0	17	..	417·7	2·332
C_2H_4 0·963	e	19·0	25	..	74·2	0·312
	f	19·0	−7	..	64·9	0·275
	g	19·0	−31	0·000	−25·5	−0·093
	h	1·0	−104	0·341	−25·5	−0·052
	i	1·0	−104	1·000	44·0	0·361
	j	1·0	17	..	79·3	0·517
CH_4 0·660	k	24·7	25	..	220·4	1·254
	l	24·7	−75·9	..	165·7	1·047
(0·636 through E_3,	m	24·7	−101·0	0·000	64·3	0·463
0·024 through E_2)	n	1·0	−161·6	0·447	64·3	0·582
	o	1·0	−161·6	1·000	132·6	1·195
	p	1·0	17	..	221·0	1·647
N_2 1·770	q	18·6	25	..	108·9	0·827
	r	18·6	−158·6	0·872	52·6	0·522
	s	18·6	−168·6	0·000	27·1	0·301
	t	1·0	−195·8	0·435	27·1	0·363
1·000	u	1·0	−195·8	0·000	6·7	0·100
0·770	v	1·0	−195·8	1·000	53·65	0·707
	w	1·0	17	..	110·0	1·056

† *f* for inhomogeneous phases denotes *quality*, i.e. the ratio of the amount of gas to the total amount of substance present.

TABLE 16. *Keesom's Nitrogen Cascade*

Thermal Equivalent of Work needed per kg. of Liquid Nitrogen

Compressor	*kcal.*
NH_3 . . .	25·6
C_2H_4 . . .	52·9
CH_4 . . .	76·3
N_2 . . .	117·7
	272·5

Effective work: $272{\cdot}5 \times 1{\cdot}7$ = 463 kcal.
= 0·539 kWh/kg.
= 2·04 kWh/gallon.

The total work, calculated as the sum of the irreversible and reversible work in Table 17, is seen to be equal to the sum of the work done by the four compressors, as shown in Table 16, within the error of calculation. Here the losses in the compressors themselves must, of course, be excluded.

TABLE 17. *Keesom's Nitrogen Cascade*
Analysis of Losses

Part	$T_0 \Delta s$ (*kcal./kg.*)
R_1	3·0
V_1	2·2
E_1	0·5
R_2	11·7
V_2	3·7
E_2	7·3
R_3	23·4
V_3	4·0
E_3	4·9
R_4	32·7
Irreversible work	93·4
Reversible work (theor.)	182·9
Total work	276·3

Summing up the results of our discussion, we come to the following conclusions:

1. The efficiency of a liquefier, as defined by the ratio of the reversible work of liquefaction to the actual power consumption, depends on the irreversible entropy increments occurring at various points in the plant. Each irreversible entropy increment ΔS leads to an additional power consumption $T_0 \Delta S$, where T_0 is room-temperature.
2. The principal sources of such irreversible entropy increase are to be found in the isenthalpic expansion of gases and, to a lesser degree, in heat transfer between gases of widely differing temperatures at the cold ends of heat-exchangers.
3. The lower the temperature of the compressed gas before its isenthalpic expansion, i.e. the nearer it is to a state of saturation, the smaller are the irreversible entropy changes involved.
4. The entropy increase occurring during the expansion of a liquid (in the course of which a part evaporates) is much smaller than in the case of a gas.
5. The low degree of irreversibility, coupled with increased refrigerating performance, makes it profitable, wherever possible, to employ refrigerants near a state of saturation.
6. The cascade system of liquefaction, an example of which was given above, constitutes a logical application of these arguments.

VI

THE PRINCIPLES OF AIR SEPARATION

1. The single column

In this chapter air will be regarded as a binary mixture consisting of 79 mole per cent. nitrogen and 21 mole per cent. oxygen. The presence of rare gases will be neglected, and it will be assumed that moisture and carbon dioxide have been removed.

It may be inferred from previous chapters that the separation of air at low temperatures involves a refrigeration as well as a distillation process. If the products are to leave the plant at room temperature, refrigeration is needed, after the initial cooling-down period, only to cover insulation losses and imperfect recuperation of cold in the exchangers. If cold liquid products are required, much more refrigeration must be provided.

It is a fundamental principle of air separation, as originally conceived by the pioneers Linde and Claude, that the air to be separated itself provides the required refrigeration. Thus, since partial condensation does not lead to a complete separation of oxygen and nitrogen, air separation combines a liquefaction plant with a rectifying column. The refrigeration is achieved by compressing the air to a suitable pressure and subsequently expanding it, either in a valve, making use of the Joule-Thomson effect, or in an expansion engine or turbine in which the air is made to do work.

The simplest form of air-separating plant is illustrated in Fig. 98, which shows the original Linde cycle first operated in 1902. Compressed air, after drying and removal of CO_2, is introduced through the heat-exchanger H, in which it is cooled by returning cold products, traverses a coil in the sump E at the bottom of the rectifying column, and is expanded to atmospheric pressure in the valve V. It is then delivered, mainly liquid, to the top of the column. The liquid descending from plate to plate becomes enriched with oxygen as a result of interaction with the rising vapours, and is partially or wholly evaporated in the sump by thermal contact with the compressed air passing through the coil. In the stationary state oxygen, either as a liquid or a gas, is continuously withdrawn from the bottom of the column and impure nitrogen vapour from the top. If no liquid oxygen is to be produced, both the nitrogen and the oxygen return through the heat-exchanger, precooling incoming compressed air. If the oxygen is withdrawn as a cold liquid, only nitrogen returns through the exchanger.

For the production of gaseous oxygen, pressures of 30–60 atm. are needed, according to the size of the plant and the quality of the insulation. If the plant is to yield liquid oxygen, the increased refrigeration requirements necessitate pressures up to 200 atm.

In order that a stationary state may be maintained, in which oxygen of required purity is continuously produced, certain conditions must be

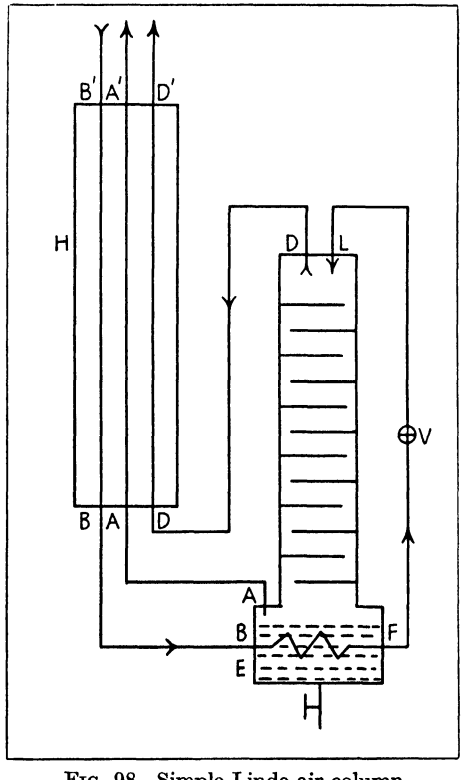


FIG. 98. Simple Linde air column

fulfilled, which can be calculated according to various methods. The procedure to be followed here is essentially that of Keesom† as it enables in principle almost all the required quantities to be obtained in a single series of operations.

The conditions for the stationary state of an air-separating plant can be ascertained by determining the following design data at certain characteristic points.

1. m rate of flow.

† W. H. Keesom, *Actes du VI^ième Congrès International du Froid*, Buenos Aires, 1932, *Rapport de la I^ère Commission*, p. 136.

2. x composition.
3. T temperature.
4. p pressure.
5. h specific enthalpy.
6. s specific entropy.

The characteristic points may, to a certain extent, be chosen arbitrarily and their total number will depend on the degree of detail that it is desired to elucidate. Many of the values are given directly by the

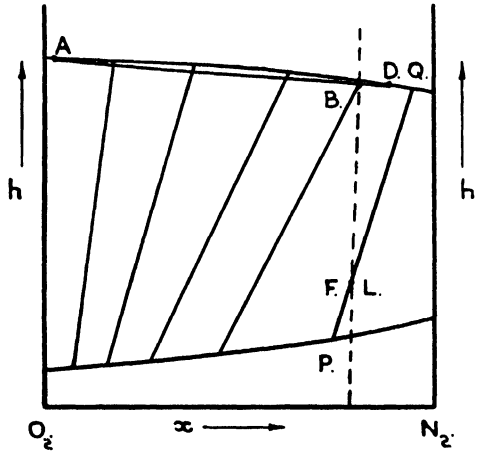


FIG. 99. Representation of simple air column on (h, x) diagram

size and requirements of the plant; others may be read off from thermodynamic charts. The rest may be found graphically with the help of simple constructions or analytically by solving certain balance equations. For the first we shall leave entropy out of account and confine ourselves to the other data.

Representation on the (h, x) diagram. First consider the column alone without the exchanger. Suppose that gaseous oxygen is to be obtained at point A (Fig. 98) with a degree of purity x_A. The nitrogen product emerges at D and air, mainly liquid, enters the column at L. The compressed air enters the sump coil at B and leaves it at F.

The (h, x) diagram of oxygen–nitrogen mixtures is shown schematically in Fig. 99 for 1 atm. pressure. It contains a dew-curve, a boiling-curve, and a series of connodals, which are at the same time isothermals. The dotted line denotes the ordinate for $x = 79$ per cent. nitrogen corresponding to atmospheric air.

The oxygen product leaves the column at A as a saturated vapour. As its degree of purity is specified, the point A can be plotted at the appropriate position on the dew-curve.

The temperature in the sump of the column is 90° K., the boiling-point of oxygen. The compressed air leaving the sump coil at F will therefore be slightly warmer than 90° allowing a temperature differential for heat transfer. We will assume that the surface of the coil is such as to allow the air to leave at 93° K. But in order to plot point F, we must know the pressure of the compressed air.

From a thermodynamic chart of air (see Figs. 85 and 86) it is apparent that the enthalpy of compressed air at 93° K. and at pressures above 5 atm. is higher than that of air at its boiling-point but depends only very slightly on the pressure. The point F can therefore be plotted preliminarily with fair accuracy on the dotted line in Fig. 99, slightly above the boiling-curve.

If the pressure is below 33 atm., the critical pressure of air, condensation takes place in the sump, and the accompanying latent heat is given up to the oxygen boiling in it. If the pressure is higher no change of phase will occur in the coil and the heat transferred to the sump will be sensible heat. It will, however, be fairly high in view of the high specific heat of air in the vicinity of its critical point. In either case the air emerging at F will have the properties of a liquid. On passing through the valve V it suffers a Joule-Thomson expansion and hence its enthalpy remains constant. Since its composition also remains the same, point L on the (h, x) diagram will be the same as point F.

At L the air is at the same atmospheric pressure for which the dew- and boiling-points are drawn in the diagram, and it can thus be seen that L lies in the inhomogeneous region, which means that a part of the air evaporates on passing through the valve. This evaporation as a result of a reduction in pressure is known as 'flashing'. The two ends of the connodal through L give the compositions of the liquid and vapour phases at L, which are, of course, not the same. The amount of flash-gas formed for each mole expanded in V is determined by the position of point L on the connodal and is equal to PL/PQ.

To determine the position of point D, which describes the state of the overhead product, consider the top plate of the column. A liquid with the composition of point P falls on this plate from above and a liquid L_2, containing more oxygen than P, leaves it to fall on to the next plate. At the best the vapour leaving the top plate will be in equilibrium with L_2. It will certainly contain more oxygen than corresponds to

point Q, the end of the connodal through L, and this itself contains more oxygen than is in equilibrium with liquid air, which is 7 per cent. at atmospheric pressure. Point D must therefore lie to the left of Q in the figure. Its exact position can be fixed only together with other characteristic points in the plant; but clearly pure nitrogen cannot be obtained with a plant of this type.

Now consider the balance of the whole column, still disregarding the exchanger, but including the expansion valve. Air enters at B, oxygen leaves at A, and nitrogen at D. Therefore, if the column is perfectly insulated, and if we use the terminology explained on p. 102, the balance reads

$$B = A+D, \tag{1}$$

the one equation standing simultaneously for the balance of mass, composition, and enthalpy. Hence B lies on the straight line connecting A and D at the point where it intersects the dotted ordinate for $x = 0{\cdot}79$.

In practice, of course, the column is not perfectly insulated and an amount of heat q leaks into it from the outside. The balance equation thus reads

$$B = A+D-q \tag{1'}$$

and point B lies lower than the point $(A+D)$ by the amount q. The main function of the air compressor is to lower the enthalpy of the incoming air so as to produce a sufficiently low enthalpy at B to cover the heat losses.

The heat transferred through the coil in the sump is given by

$$Q_E = B-L = m_B(h_B-h_L). \tag{2}$$

For every mole of air entering the column, Q_E is therefore equal to the distance from B to L.

Neglecting heat losses in the exchanger, the balance of this unit reads

$$B'-B = A'-A+D'-D. \tag{3}$$

It may be assumed that the air-inlet temperature is fixed and that the surface of the exchanger is so chosen as to leave a certain temperature difference between air and products at the warm end. If A and D are assumed to be known from the previous discussion, the whole right-hand side of this equation is determined. But the enthalpy of B is also known from the balance of the column. Hence the enthalpy of B' can be ascertained and the pressure looked up on a thermodynamic chart of air. It is then possible to ascertain the power consumption by calculating the work required to compress the air to this pressure. At room-temperature and up to moderate pressures, air is not far removed from a perfect gas

and the work may be determined as

$$W = nRT \log p_B \tag{4}$$

and multiplied by a factor which accounts for the deviation of actual compression from the isothermal and the mechanical losses in the compressor. In the case of multi-stage compression, in which each stage is substantially adiabatic, the work is best determined directly from the (T, s) diagram of air. In this case only the mechanical efficiency of the compressor has to be taken into account, which is generally taken as about 0·66.

Determination of theoretical plates. It has been shown that the single column arrangement here under discussion cannot lead to a pure nitrogen product. In order that it may produce pure oxygen, certain conditions must be fulfilled within the column which can again be demonstrated with the help of the (h, x) diagram.

We shall assume at this stage that vapour and liquid actually attain equilibrium on every plate. In practice this will not occur and the efficiency of plates will be considered in some detail in Chapter VIII. A plate on which complete equilibrium is reached is known as a 'theoretical plate' and we shall now determine the number of theoretical plates required in a single air column to produce oxygen of a specified purity. It will be assumed further that no interaction takes place between liquid and vapour except on the plates themselves.

In Chapter IV we introduced the concept of equivalent current as the difference between the liquid and the vapour phase in a section of a separator, and we showed that the equivalent current is a constant throughout the unit. Thus, if L_n and G_n are the liquid and gaseous phases passing a section above the nth plate, we can write the equations

$$L-D = L_1-G_1 = L_2-G_2 = L_n-G_n = \ldots = Z. \tag{5}$$

But the balance of the column as a whole (Fig. 98) gives

$$L-D = A-Q_E \tag{6}$$

so that

$$Z = A-Q_E, \tag{7}$$

which means that $x_Z = x_A$. So we can plot Z as the point of intersection of the straight line LD and the ordinate through A, and all the straight lines $L_n G_n$ will pass through Z (see Fig. 100).

Now D is the gas leaving the top plate. According to our assumption, the liquid L_2 leaving the first plate will be in equilibrium with $G_1 = D$. So on the (h, x) diagram we can plot L_2 as the lower end of the connodal through D. If we now join ZL_2 and produce to the vapour curve, the

point of intersection will give G_2, and L_3 is the lower end of the connodal through G_2. Evidently this operation can be continued until some vapour phase G_n coincides with or passes A. The number of steps is equal to the number of plates needed.

We see at once that this construction is feasible only if the slopes of

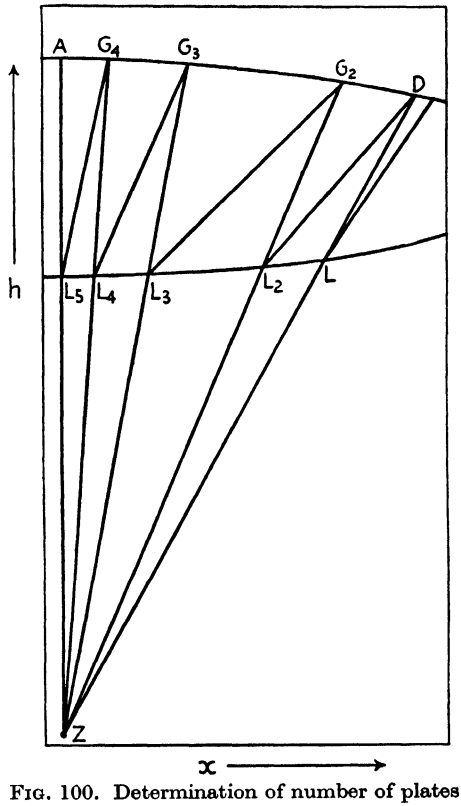


FIG. 100. Determination of number of plates in simple column

the lines $ZL_n G_n$ are steeper than the connodals. If a connodal coincided with one of these lines we should not be able to move across the figure. More especially, if LD coincided with the connodal through L we should be unable to start. This brings out very clearly the fact, already noted, that D must contain less nitrogen than is in equilibrium with L.

Moreover, the steeper LD is, compared with the connodal through L, i.e. the impurer the nitrogen product, the farther the first and every subsequent step will take us in the direction of A. That is to say, the fewer plates will be needed to obtain a given degree of oxygen purity.

If the number of plates is less than that found graphically by this method, we shall not be able to obtain oxygen of the desired concentration without making the nitrogen impurer than was stipulated.

EXAMPLE. 10 cu. m. per hour of 99 per cent. gaseous oxygen are to be produced in a single-column plant operating at 1 atm. abs. The nitrogen product is to contain 91 per cent. of nitrogen. The air is assumed to enter the exchanger at 290° K. and the outgoing products leave at a temperature 4° lower. The heat losses through the insulation are to be taken as 3·0 kcal. for each cu. m. of air treated, of which 2·2 kcal. leak into the column and 0·8 kcal. into the exchanger.

1. How much air must be compressed?
2. What is the oxygen yield?
3. To what pressure must the air be compressed?
4. At what temperature does the air leave the exchanger?
5. How much heat is exchanged in the evaporator?
6. How many theoretical plates are needed?
7. What is the power consumption?

1. Using the same lettering as in Fig. 98, the balance of mass and composition give

$$m_B = m_A + m_D,$$

$$m_B x_B = m_A x_A + m_D x_D.$$

With $m_A = 10$, $x_B = 0{\cdot}79$, $x_A = 0{\cdot}01$, and $x_D = 0{\cdot}91$, we obtain

$$m_B = 75 \text{ cu. m./hr.}$$

2. The amount of oxygen available is thus $0{\cdot}21 \times 75 = 15{\cdot}75$ m.³/hr., and the amount of oxygen produced is $0{\cdot}99 \times 10 = 9{\cdot}9$ m.³/hr. The *oxygen yield* is thus $9{\cdot}9/15{\cdot}75 = 63$ *per cent.*

3. The balance of the whole plant can be written

$$A' + D' = B' + Q,$$

where Q denotes the total heat loss. Hence

$$m_{A'} h_{A'} + m_{D'} h_{D'} = m_{B'} h_{B'} + Q.$$

Assuming that, at low pressures and around room-temperature, the enthalpy of oxygen–nitrogen mixtures is a linear function of composition, the left-hand side of this equation is equal to the enthalpy $m_{B'} h'$ of $m_{B'}$ m.³ of air at 1 atm. and 286° K. Hence

$$h' = h_{B'} + Q/m_B$$

and h' can be found from a thermodynamic chart of air to be 124·5 kcal./kg. Q/m_B is given as 3·0 kcal./cu. m., which is equal to 2·5 kcal./kg. of air. Hence $h_{B'} = 124{\cdot}5 - 2{\cdot}5 = 122$ kcal./kg.

Since the air enters the plant at 290° K., it has to be compressed to a pressure at which its enthalpy at this temperature is reduced to 122 kcal./kg. Reference to a thermodynamic chart shows this pressure to be *60 atm.*

4. To find the condition of the air at the cold end of the heat-exchanger, consider the heat balance of the column

$$B+Q_1 = A+D,$$

where Q_1 is the heat loss to the column

$$m_B h_B+Q_1 = m_A h_A+m_D h_D.$$

Q_1/m_B is given as 2·2 kcal./m.³ of air. m_A, m_B, and m_D are known. h_A and h_D can be found from the (h,x) diagram of oxygen–nitrogen mixtures. h_B is thus the only unknown and it is found that

$$h_B = 72{\cdot}8 \text{ kcal./kg. air.}$$

For this enthalpy, the temperature at 60 atm. is found to be

$$T_B = 149° K.$$

5. The temperature of the air leaving the evaporator coil can be taken as 94° K., i.e. slightly higher than that of the oxygen boiling in the evaporator. The enthalpy of air at 60 atm. and 94° K. can be read off as 34 kcal./kg. The enthalpy of the air entering the coil was found in (4) to be 72·8 kcal./kg. The heat transferred in the coil is therefore 72·8—34 = 38·8 kcal./kg. or, for 75 cu. m./hr., *3,520 kcal./hr.*

6. By plotting B, D, and A on the (h,x) diagram, joining DB and producing to $x = x_A$, we find point Z and can carry out the construction described above. We find that *7 theoretical plates* are required.†

7. Taking air as a perfect gas, the theoretical work of isothermal compression $NRT \log p_2/p_1 = 0{\cdot}85$ kWh/cu. m. of oxygen. Assuming the compressor efficiency as compared with the isothermal to be 0·55, we arrive at a practical power consumption of *1·55 kWh/m.³* of oxygen. To produce 10 cu. m. of oxygen per hour the plant therefore needs *15·5 kW or 21 B.H.P.*

Reversible and irreversible work of separation. The work W of separating air into pure oxygen and impure nitrogen is simply the work of compressing the air to the required pressure, and this, as we have seen, is given by the conditions of the plant. W is usually very much greater than the theoretical work $W_{rev} = 0{\cdot}067$ kWh/cu. m. of pure oxygen, which would be needed if the process were completely reversible and which may be computed from formula (18) on p. 111. Part of this discrepancy

† The number of theoretical plates is actually greater owing to the argon content of the air, as will be shown in Chapter VIII.

is due to the low efficiency of the compressor and to the fact that the compression is in reality not isothermal but approximately adiabatic. In practice the work done by the compressor is from 1·6 to 1·7 times as great as it would be for the case of isothermal compression and an efficiency equal to unity. But this only covers a fraction of the difference between W_{rev} and W.

A further source of additional work is due to the heat leakage into the column and exchanger from the environment. This heat leakage, as we have seen, requires refrigeration so that the stationary state may be maintained, and refrigeration demands work. The removal of an amount of heat Q_0 at a temperature T_0 and its disposal at a temperature $T_1 > T_0$ necessitates the expenditure of an amount of work W', so that

$$W' \geqslant Q_0 \frac{T_1 - T_0}{T_0}.$$

An accurate calculation of W' is complicated by the fact that the heat Q is imparted to the plant throughout its whole extent, that is to say, at various temperatures. However, we can usually obtain a fair approximation by separating Q into two parts, as was done above, and assuming one part to enter the column and the other the exchanger. In the case of air the difference in temperature between the top and bottom of the column is small compared with that between the column and the environment, so that we shall not go far wrong in taking the mean temperature of the column as a whole. In taking the mean temperature of the exchanger we must remember that the heat flux per unit surface is the greater the lower the temperature.

But there is yet another source of work, and this is due to irreversible changes occurring within the column. In Chapter IV we showed that such a change, which leads to an increase in entropy ΔS_{irr}, requires the expenditure of an amount of work equal to $T_0 \Delta S_{irr}$, where T_0 is the temperature of the surroundings, in our case room-temperature, at which this work must be performed. Moreover, we pointed out how ΔS_{irr} may be determined graphically with the help of the (h, s) projection if the corresponding points on the (h, x) plane are known.

Now in a rectifying column the equivalent currents undergo irreversible changes, as described in Chapter IV. Every time the current passes through a plate and when it enters or leaves the evaporator, a transfer of matter and heat occurs between the liquid and the vapour, in that the two phases are brought to, or close to, equilibrium with each other. Since these processes are irreversible, they entail an increase of

entropy ΔS_{irr}. After what we have said in Chapter IV, there will be no difficulty in evaluating ΔS_{irr} and the corresponding W_{irr} for the evaporator and for each plate.

In Fig. 101 the (h, x) diagram of Fig. 99 is shown in conjunction with the corresponding (h, s) diagram. The points L, A, D, G_n, L_n, etc., on the latter may be determined graphically from the corresponding points

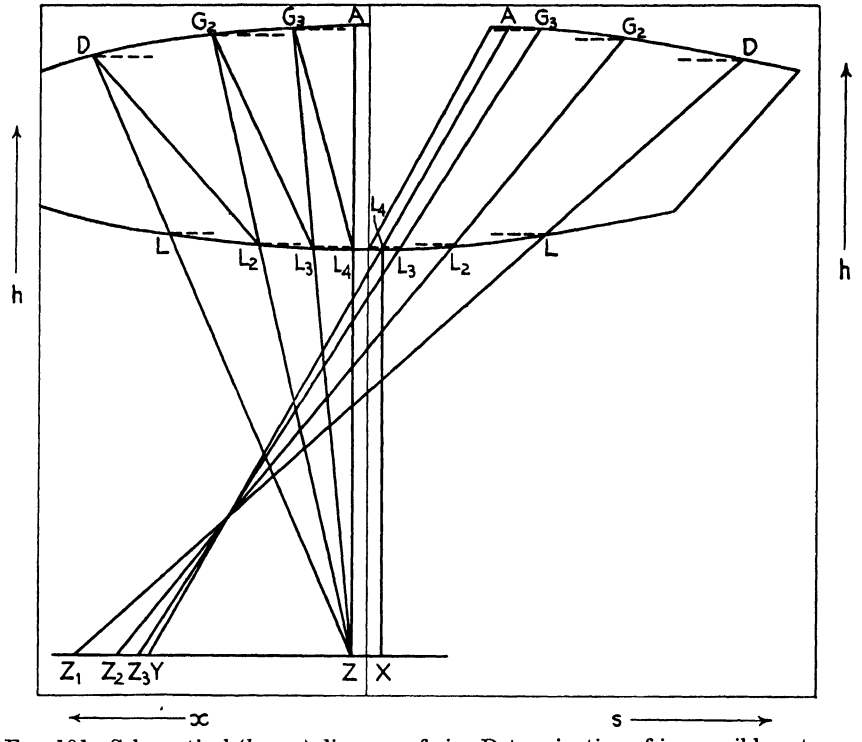


FIG. 101. Schematical (h, x, s) diagram of air. Determination of irreversible entropy increments

on the former since they are situated on the boundary curves and have the same values of h. Whereas the projections of the straight lines DL, G_2L_2,... on the (h, x) diagram all intersect in Z, the corresponding lines in the (h, s) projection will not meet in a single point, but will intersect the horizontal line $h = h_Z$ at different points $Z_1, Z_2, \ldots$. Since the process occurring on a plate is adiabatic (except for heat leaks, which may here be neglected), $\Delta S = \Delta S_{\text{irr}}$. Therefore the distance between two adjacent points Z_n and Z_{n-1} gives the irreversible change of entropy Δs_{irr}, incurred by unit mass of equivalent current on passing the plate.†

† From here on, since we shall be referring to distances on the (h, s) diagram, i.e. to *specific* quantities, we shall use small letters.

It should be noted that Δs_{irr} must always be positive in the direction of actual flow. Thus, if the current is defined as $L-G$, as is usually the case, when $m_L > m_G$, and if the plates are numbered from the top downwards, s_n must be greater than s_{n-1}.

To determine Δs_{irr} for the evaporator, we must remember that here the process is not adiabatic, but that an amount of heat q is transmitted to the liquid from without. This leads to a reversible increase of entropy equal to q/T_e, where T_e is the temperature in the evaporator. The total increase of entropy will thus be

$$\Delta s = q/T_e + \Delta s_{\text{irr}},$$

so that

$$\Delta s_{\text{irr}} = \Delta s - q/T_e.$$

Now consider the straight line on the (h, s) diagram corresponding on the (h, x) side to the line AZ. Suppose this line to intersect the liquid branch on the (h, s) side in L_4 and the line $h = h_Z$ in Y, and let the line $s = s_{L_4}$ intersect $h = h_Z$ in X. The entropy of the equivalent down-current which enters the evaporator from the last (third) plate will be s_{Z_3}. Then $\Delta s = Z_3 X$ and, since $(\partial h/\partial s)_p = T$ and $L_4 X = q$,

$$\Delta s_{\text{rev}} = q/T_e = XY.$$

Therefore

$$\Delta s_{\text{irr}} = Z_3 Y.$$

We have thus determined not merely the total irreversible increase of entropy in the column, which is the length of $Z_1 Y$, but, marked off along this line, we have obtained the increase of entropy due to irreversible processes occurring on each plate separately and in the evaporator. So we can tell how much additional work $w_{\text{irr}} = T_0 \Delta s_{\text{irr}}$ is occasioned by irreversible changes occurring at each point of the column.

2. The double column

The simple rectifying column has two essential disadvantages. The first is that it can produce pure oxygen only. The nitrogen, as we have seen, is always more or less impure. In the early days of air separation, when nitrogen was of no commercial value, this might hardly have been felt as a drawback. The second disadvantage must have appeared far more serious: large quantities of precious oxygen were wasted. Consider a column producing oxygen of practically 100 per cent. purity and the purest nitrogen obtainable, viz. 93 per cent. Let L be the mixture entering the column and A and D the oxygen and nitrogen products respectively, and suppose 1 cu. ft. to enter the plant in a

given time. Then

$$m_A + m_D = 1, \qquad 0{\cdot}07m_A + 0{\cdot}93m_D = 0{\cdot}79.$$

It follows that $m_D = 0{\cdot}83, \qquad m_A = 0{\cdot}17.$

The actual amount of oxygen passing through the column is

$$m_0 = 0{\cdot}21.$$

Thus 4/21 = 19 per cent. of this oxygen passes out with the nitrogen and is lost. The production of 1 cu. ft. of oxygen therefore consumes more energy than it would if all the oxygen contained in the air were extracted from it.

From the general concepts developed in the preceding chapters we may infer that a liquid and a vapour conducted over plates in counter-current can in principle be made to separate into pure components, and if our column is unable to accomplish this, the reason is that it is only half a column. The liquid introduced at the top is indeed rectified as it falls from plate to plate, but the vapour rising from the first plate is simply ejected without further treatment. In order to complete the process, this vapour should be led over more plates and there meet a liquid richer in nitrogen.

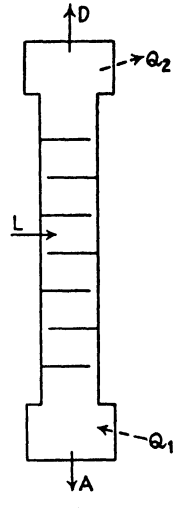


FIG. 102. Development of the double column. First step

A complete column should therefore be a symmetrical piece of apparatus, as shown schematically in Fig. 102 (see also Fig. 62, Chapter III, p. 79). The air would enter in the middle of the column, or rather at a point corresponding to its composition. The evaporator below, in which a quantity of heat Q_1 is transmitted to the liquid, should have its counterpart in a condenser at the top, from which a quantity of heat Q_2 is withdrawn. While liquid oxygen is evaporated below, gaseous nitrogen should be condensed above. An apparatus of this type should produce both components in the pure state.

In distilling oil and alcohol this type of column is actually employed. We must now show why it is inapplicable to air separation. In stills functioning at temperatures above that of the environment, heat is introduced with the help of steam or hot gases heated in a furnace and is withdrawn by means of cooling water. The quantities of heat introduced and withdrawn are completely independent of one another, and the temperatures required, being above room-temperature, can always be maintained without the expenditure of mechanical energy. But the separation of air is carried out below room-temperature and the

low temperatures must be maintained with the help of refrigerating machinery. Though when the products are finally obtained at room-temperature the sum total of refrigeration vanishes, except for what is needed to compensate for losses, we still require a device to enable us to transfer quantities of heat at certain specified low temperatures. Moreover, in air separation the only refrigerating agent at our disposal is air itself and its products oxygen and nitrogen. If heat is to be withdrawn at a definite temperature, this can be effected only if air, oxygen, or nitrogen can be brought into and maintained in such a state in which they can absorb heat at this temperature. But even if this is possible, the amount of refrigerant available is limited and given by the amount of air passing through the plant, unless auxiliary refrigerating cycles are employed, in which the air is not separated.

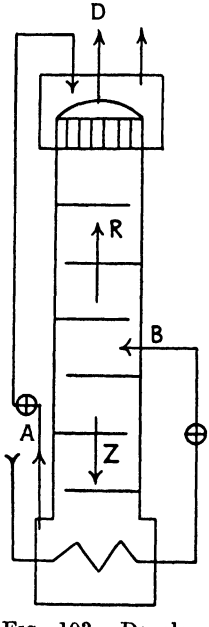


FIG. 103. Development of the double column. Second step

Now in a column of the kind shown in Fig. 102 the gaseous nitrogen must be condensed at its boiling-point, and this will be the coldest part of the column. Moreover, the temperature of the refrigerating agent must be somewhat lower than that of the substance which is being condensed.

What refrigerant is available at a temperature below the boiling-point of nitrogen? We might think of using liquid nitrogen itself, boiling at reduced pressure. But liquid nitrogen is not available; for the nitrogen reaches the condenser as a vapour and we should first have to condense it. The latent heat of evaporation of the nitrogen thus liquefied would therefore have to be employed to condense this same nitrogen, and we cannot use it again to maintain a reflux in the column.

The only refrigerant at our disposal is the liquid oxygen formed in the evaporator, which could be transferred to the condenser, as shown in Fig. 103. In order to make use of it, we must arrange for the column to produce *liquid* oxygen, apart from the vapour emitted from the evaporator to rectify the liquid air. But the temperature of liquid oxygen (90° K.) is 13° higher than that of boiling nitrogen, that is to say, about 16° higher than the temperature needed to liquefy nitrogen in the condenser. To bring the temperature of liquid oxygen down to 74° K. we should have to lower its vapour pressure to about 9 cm. of mercury. This is impracticable. It is far easier to raise the temperature

of boiling nitrogen by increasing the pressure in the column. At 5 atm. abs. the boiling-point of nitrogen is about 94° K., which is well above the boiling-point of oxygen at atmospheric pressure.

Accordingly, the next step towards a plant that will yield pure oxygen and pure nitrogen simultaneously is *to raise the pressure in the column to about 5 atm. abs.*

But this is only one step; for a column of the type shown in Fig. 103 cannot yield both products in a pure state.

Suppose that Fig. 104 represents the (h, x) diagram of oxygen–nitrogen mixtures at 5 atm. pressure. The air is admitted to the column of Fig. 103 at B, either as a liquid or as a vapour or, in the general case, as a mixture of liquid and vapour. In Fig. 104 B is plotted on the liquid branch. Gaseous nitrogen is removed at the top of the column at D and liquid oxygen at A. There will then be an equivalent up-current $R = G - L$ in the upper part of the column and an equivalent down-current $Z = L' - G'$ in the lower part. The balance of a section of the column including the inlet B will thus read

$$B = Z + R.$$

The points Z and R on Fig. 104 will thus lie on a straight line through B. But at the top of the column we have

$$R = D - Q_2,$$

where $-Q_2$ is the amount of heat withdrawn in the condenser, and at the bottom of the column

$$Z = A - Q_1,$$

where Q_1 is the heat introduced into the evaporator. Therefore

$$x_R = x_D \quad \text{and} \quad x_Z = x_A.$$

So R is on the line $x = x_D$ and Z on the corresponding line $x = x_A$, where x_D and x_A are the specified compositions of the 'pure' products.

Now let BB' be the connodal through B. In order that rectification may proceed, RBZ must be steeper than BB'. This can be proved in exactly the same way as we proved the corresponding rule in the case of the simple column. If BB' and RZ lie on one straight line, rectification will require an infinite number of plates. So the line $Z'BB'R'$ is

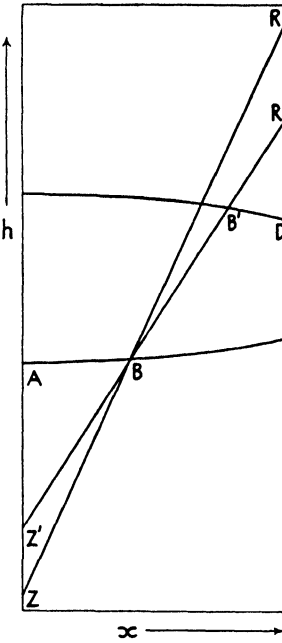


FIG. 104. Limiting line for double column

the line of limiting slope. But $R'D = Q_2/m_D$ and $Z'A = Q_1/m_A$ give the minimum amounts of heat required to be withdrawn from the condenser and introduced into the evaporator respectively per unit mass of D and A.

Now suppose that we wish to obtain very pure oxygen and at the same time very pure nitrogen; for the purpose of this argument we may put $x_D = 100$ per cent. N_2, $x_A = 0$ per cent. N_2. We shall assume the separation to be effected at 5 atm. pressure and the mixture to be introduced at B as a boiling liquid, which is in fact the most advantageous condition. Then B will lie on the liquid boundary curve at $x_B = 79$ per cent. The connodal through this point, on being produced behind B', intersects the ordinate axis $x = 100$ per cent. at R', and, referring to the accurate (h, x) diagram for 5 atm., we find

$$h_{R'} = 2{,}580 \text{ cal./mole.}$$

Similarly, we obtain $$h_D = 1{,}707 \text{ cal./mole.}$$

Therefore $$R'D = Q_2/m_D = \quad 873 \text{ cal./mole.}$$

This is the amount of heat which must be withdrawn from the condenser for every mole of nitrogen passing out of the column. Now if both the products are pure, every mole of air entering the column must produce 0·79 mole of nitrogen at D. So for every mole of air to be separated we must withdraw

$$Q_2 = 0{\cdot}79 \times 873 = 690 \text{ cal.}$$

from the condenser. All that we have at our disposal to absorb these 690 cal. is the pure liquid oxygen removed at A and expanded to atmospheric pressure in a valve without change of enthalpy. The latent heat of evaporation of 1 mole of oxygen at 1 atm. pressure is $\lambda_{O_2} = 1{,}632$ cal., and for every mole of air we have 0·21 mole of oxygen. Accordingly, we have at our disposal a refrigerating capacity

$$Q_2' = 0{\cdot}21 \times 1{,}632 = 343 \text{ cal.},$$

which is only half as great as that needed.

This proves that pure oxygen and pure nitrogen cannot be obtained simultaneously in a column of this type.

If we keep to our demand for pure nitrogen, we can see what kind of oxygen this column will give us. Let $x_A = 40$ per cent. N_2. We then have

$$m_A + m_D = 1, \qquad 40m_A + 100m_D = 79.$$

It follows that $$m_D = 0{\cdot}65, \qquad m_A = 0{\cdot}35.$$

Then the amount of refrigeration needed is

$$Q_2 = 0{\cdot}65 \times 873 = 568 \text{ cal.},$$

and the amount of refrigeration available is

$$Q'_2 = 0{\cdot}35 \times 1{,}632 = 571 \text{ cal.},$$

so that Q'_2 just covers Q_2.

If we wish to obtain pure nitrogen with a single column having a condenser and working at 5 atm. pressure, the richest oxygen product obtainable will contain no more than 60 per cent. O_2. In fact it will contain less as the column has a finite number of plates and because not the whole of λ_{O_2} is available. Part of the liquid oxygen evaporates on passing through the valve.

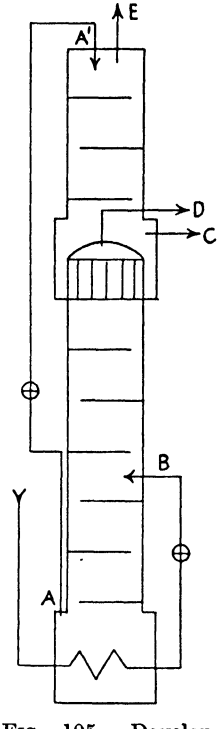


FIG. 105. Development of double column. Third step

In order to obtain pure oxygen and nitrogen simultaneously the impure oxygen product emerging at A will have to be further purified before it is introduced into the condenser. *This can be done by introducing a set of plates between the inlet A' and the condenser*, so as to rectify the liquid mixture. This brings us another step forward to Fig. 105, in which pure oxygen may be withdrawn from the condenser-evaporator at C and pure nitrogen at D. But this, too, is only a partial solution; for though we may indeed obtain pure oxygen and pure nitrogen at the same time, we shall still lose the vapour emerging at E, which will contain at least as much oxygen as is in equilibrium with the liquid delivered at A'. In fact, we seem to have moved in a vicious circle and to have come back to the same point which determined the inadequacy of the simple column. For we must now again find a refrigerant that will furnish us with liquid nitrogen to rectify this vapour.

However, this difficulty can be overcome fairly easily. We have seen that liquid nitrogen cannot be made to reproduce itself *and* simultaneously to maintain a reflux in the column. But now the reflux is maintained by the oxygen product and all we require of the nitrogen is self-reproduction. *If we prolong the upper column* (Fig. 105) *above A' and withdraw liquid nitrogen at D, we can deliver this liquid nitrogen at*

the summit of the column, allow it to rectify the vapour rising at E which is thereby gradually transformed into oxygen, and finally evaporate it again in the condenser, thus renewing the liquid at D.

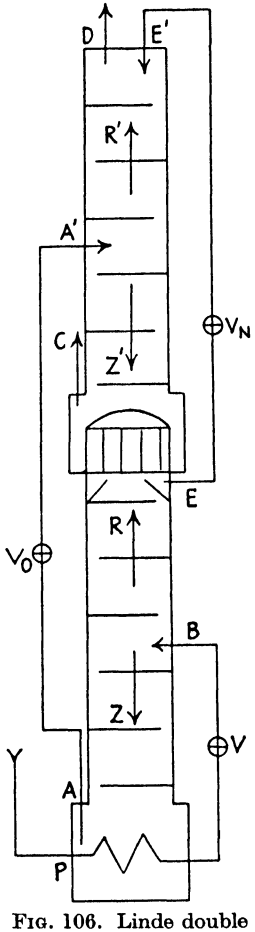


FIG. 106. Linde double air column

This brings us at length to the complete double column, as shown in Fig. 106, which was evolved by Linde in 1910 and which still predominates in air separation. It appears now as a logical development from first principles, and its prevalence throughout thirty years of technical evolution indicates that the solution was indeed satisfactory.

The final cycle may be summed up as follows: Compressed air, precooled in a heat-exchanger, enters the evaporator coil at P, is expanded to 5 atm. pressure in the valve V, and delivered to the middle of the lower column at B. Here it is separated into pure liquid nitrogen and a liquid containing about 38 per cent. of oxygen. The latter is withdrawn from the lower column at A, expanded to atmospheric pressure in the valve V_0, and admitted in the middle of the upper column at A'. The liquid nitrogen collects in the trough below the condenser, whence it is removed at E, expanded to atmospheric pressure in the valve V_N, and admitted at the top of the upper column at E'. Finally, gaseous oxygen is withdrawn immediately above the condenser at C and gaseous nitrogen at D.

Neglecting the heat losses for the time being, the balance equations for the various parts of the column can be read from Fig. 106 as follows:

(*a*) Re-boiler $P-B = A-Z$

(*b*) Condenser-Evaporator $R-E = C-Z'$

(*c*) Lower Column Feed $B = R+Z$

(*d*) Upper Column Feed $A' = R'+Z'$

(*e*) Top of Upper Column $R' = D-E'$.

If these five equations are added together, noting that $A' = A$ and $E' = E$, the result is $P = C+D$ which gives the total balance of the column.

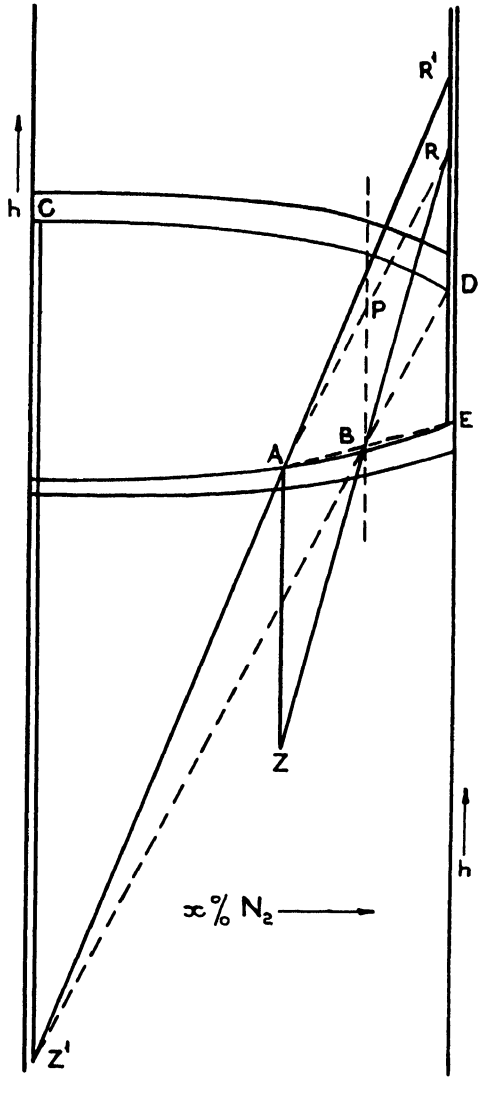


FIG. 107. Representation of double air column on (h, x) diagram

The process is represented graphically in Fig. 107 in which the (h, x) curves for 5 and 1 atm. are superposed. B lies, as in the single column, slightly above the boiling-curve for 5 atm. at $x_B = 79$ per cent. N_2. At B the air separates into an equivalent down-current Z and an equivalent up-current R. The composition of the oxygen-enriched

liquid at A can be chosen arbitrarily between rather narrow limits, as will be shown later. It is generally close to 62 per cent. N_2. Z must lie vertically below A, and R vertically above E. At A', which on the diagram is the same point as A, the enriched air separates into the equivalent currents Z' and R', and Z' must lie directly below C, the point describing the state of the oxygen product. However, R' will not lie directly above the point D for the nitrogen product. According to equation (e), R' lies on the extension of the line $E'D$, which is in general not vertical, as the nitrogen vapour leaving at D will be purer than the liquid nitrogen introduced at E'. If the nitrogen product is to be very pure, the difference between x_D and $x_{E'}$ is small and it will be neglected for the purpose of this calculation, which is to derive a simple construction to determine the approximate positions of the points Z, R, Z', R'.

Equations (a) and (c) give $P = A+R$, showing that these three points are on a straight line.

(d) and (e) give $Z'+D = A'+E'$, and since A' and E' must add up to atmospheric air, Z' and D must do the same.

Fixing A at 62 per cent. N_2, we can draw AE and, through the point where it cuts the ordinate for 79 per cent. nitrogen, draw DZ', thus fixing Z'. Then through Z' and A we can draw $Z'AR'$ fixing R'. R can be fixed by drawing APR, and finally Z by drawing RBZ.

The position of point A (A') is limited in both directions. Since Z' is very nearly independent of A, a shift of x_A to higher nitrogen concentrations reduces the slope of the line $Z'AR'$ and, at a certain value of x_A, this line coincides with the connodal through A'. This position corresponds to the minimum reflux ratio for the upper column and thus gives the maximum nitrogen concentration of x_A. If A moves to higher oxygen concentrations, the line APR becomes flatter and R falls. Thus the slope of RBZ decreases and, at a certain minimum value of x_A, coincides with the connodal through B. This position corresponds to the minimum reflux ratio in the lower column. If the lower column works at 5 atm. and the upper at 1 atm. and if both products are to be substantially pure, the theoretical limits of x_A for a small plant lie at 57 and 67 per cent. nitrogen. Practically x_A can vary between 60 and 64 per cent.

The preceding discussion shows that, apart from a slight variability in the position of point A, all the characteristic points of a double-column air-separating plant are determined by the required purity of the products and the heat losses incurred by leakage through the lagging and imperfect recuperation in the exchanger. For it is these losses

which determine the pressure to which the air must be compressed and the final position of the points P and B. In particular the heat transferred in the re-boiler and the condenser-evaporator is fully determined, since the former is given by $Z-A$ and the latter by $R-E$ $(= C-Z')$. This illustrates the important difference between an air-separation plant and a conventional distillation plant, in which the reflux ratio, and hence the heat supplied to the re-boiler and withdrawn from the condenser, can be varied within very wide limits. This is clearly connected with the fact that in an ordinary fractionating tower the re-boiler is heated with steam or hot gases and the condenser cooled with water, while in the plant here under discussion the re-boiler heat and the cold needed to supply reflux in both columns have to be provided from the same air which is being separated into its components.

The number of theoretical plates required in each section of the two columns can be determined in the same way as in the case of the single column, as described in § 1 of this chapter. The same construction can also be used to ascertain the irreversible entropy increases on each plate and in the condenser and re-boiler.

Now since the heat losses determine the pressure to which the air must be compressed, they naturally also determine the power consumption since the power is used to compress the air. As it is the losses that cause the refrigeration requirements, their connexion with the power consumption seems obvious. However, if we recall that all the characteristic points in the plant are fixed by the initial pressure and hence by the heat losses, it becomes evident that the irreversible entropy increases on the plates and in the other parts of the plant are also fixed in the same way. The additional work which is required to compensate for these irreversible entropy increases must therefore be the same work that is needed to overcome the cold losses, i.e. to supply the refrigeration. Compression of a gas at constant temperature reduces its entropy as well as its enthalpy.

We are thus at liberty to consider this work as a means either of providing refrigeration by reducing enthalpy, or of compensating for irreversibilities by reducing entropy. The effect is ultimately the same.

The following example may serve to illustrate this point. Consider a small double-column air-separating plant, in which the heat losses are such as to require an operating pressure of 60 atm. Suppose the required products to be 98 per cent. oxygen and 98 per cent. nitrogen, both as gases at room-temperature. The balance of mass and composition shows that, for every cu. m. of oxygen product, 5·06 cu. m. of

air have to be compressed. The isothermal compression of this air requires theoretically 0·580 kWh or, with a compressor efficiency of 60 per cent., 0·97 kWh/cu. m. O_2.

Now if we determine the irreversible entropy increments incurred at all points in the plant, and add to this figure the reversible entropy of mixing, the result must give us the total decrease in entropy ΔS that we have to bring about to separate the air. If T_0 is the temperature of the environment, $T_0 \Delta S$ should again give us the total theoretical power consumption.

This calculation has actually been carried out in the way indicated earlier in this chapter. The figures are not very accurate as they involve adding up a large number of very small distances on the (h, s) diagram. The results were as follows:

TABLE 18. *Entropy Increments in Small Two-column Air-separating Plant*

Units: g. cals./°C. mol. oxygen product (98%)

Lower Column above feed	0·96
Lower Column below feed	2·13
Upper Column above feed	5·70
Upper Column below feed	4·00
Heat Exchanger	9·10
Main Expansion Valve	3·68
Nitrogen Expansion Valve	0·96
Rich Air Expansion Valve	1·60
Re-boiler	11·40
Condenser-Evaporator	0·20
Reversible entropy of mixing	5·02
Total entropy decrement	44·75
Theoretical work (T_0 = 288° K.)	12,880 g.cals./mole = 531 kcals./cu. m. = 0·618 kWh/cu. m.
Efficiency of compressor.	60%
Final power consumption	1·03 kWh/cu. m.
Actual power consumption	0·97 kWh/cu. m.
Deviation	6%

The agreement between the two values is probably as good as can be expected from the accuracy of the determinations.

VII

COMMERCIAL AIR SEPARATION

1. Linde plants with process and refrigerating cycles

In the example treated in the last chapter, it was found that the air had to be compressed to about 60 atmospheres to maintain a stationary state in a double column when producing oxygen and nitrogen. This compression required a power consumption of about 1·0 kWh/cu. m. of oxygen produced, which is a great deal higher than the 0·02 kWh/cu. m. theoretically necessary. In commercial oxygen plants power consumption is a very important part of the cost of the product and it is essential to keep the figure as low as possible. Some reasons for the discrepancy between theoretical and practical figures have already been mentioned, but a fuller analysis is necessary in order to understand how the problem of reducing power consumption is being tackled.

The pressure of 60 atm. was arrived at by calculating the enthalpy at which the air must enter the plant at room temperature. This enthalpy had to be smaller than the combined enthalpy of the products leaving the plant by an amount equal to the total cold losses, and the only way to reduce the enthalpy of a gas at constant temperature is by increasing its pressure.

The heat losses were seen to be of two kinds:

1. Losses through ingress of heat through the lagging;
2. Losses through imperfect recuperation in the exchanger, as a result of which the products leave at a temperature somewhat lower than the incoming air.

Since at low pressures and relatively high temperatures the enthalpy of air decreases very slowly with increasing pressure, as may be seen from the (h, T) and (T, s) diagrams on Figs. 85 and 86, it is necessary to compress the air to about 60 atm. in the case of a fairly small plants in order to compensate for the heat losses. In larger plants, where the surface is smaller relative to the amount of gas passing, the heat losses for every cu. m. of air treated are correspondingly smaller and the pressure required is therefore lower. Very good insulation and very efficient heat exchangers naturally lead to a decrease in heat losses and hence to lower pressures, a lower power consumption and cheaper oxygen and nitrogen; but a limit is soon reached at which the insulation becomes so thick and unwieldy and the heat exchangers so large, heavy, and expensive, that further improvement becomes uneconomical.

However, in theory we can imagine a plant that is so perfectly insulated and has such an efficient exchanger that only a very low compression pressure would be necessary. On the other hand, the double-column process is based on the fact that the pressure in the lower column is higher than that in the upper column by an amount at least equal to, and in practice greater than, the difference in vapour pressure between oxygen and nitrogen. Otherwise it would not be

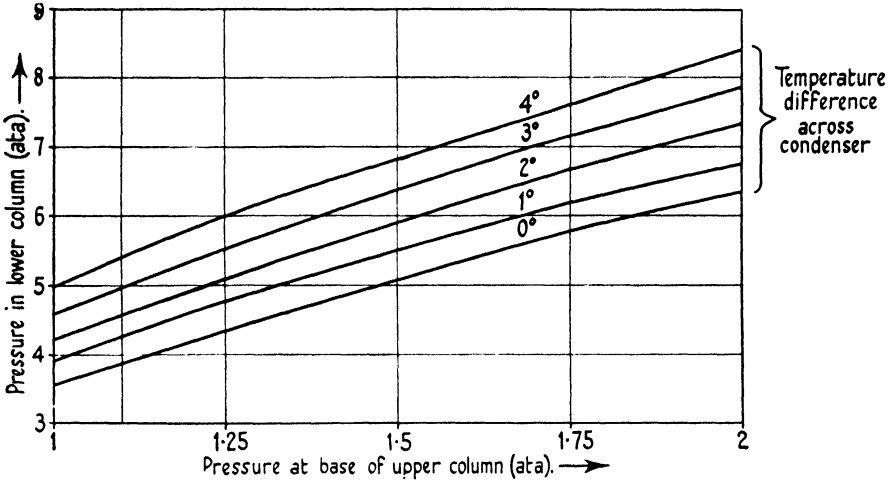


FIG. 108. Pressure in lower air column as a function of pressure in upper column and temperature difference across evaporator-condenser

possible to condense nitrogen at the top of the lower column with the help of oxygen boiling in the upper column. It has been said that the pressure in the lower column is in practice about 5 atm. when the upper column works just above atmospheric pressure. At the normal boiling-point of oxygen, the vapour pressure of nitrogen is 3·6 atm. and this is therefore the lowest theoretical pressure at which the lower column can possibly run. The pressure must, in effect, be higher because a temperature difference must be maintained across the surface of the condenser-evaporator, and because the upper column must have a pressure somewhat above 1 atm. to enable the products to overcome the resistance of the fractionating plates and the heat-exchangers. Fig. 108 shows how the operating pressure in the lower column depends on these two factors. Evidently the compression of the air to approximately 5 atm. is needed, not only to lower the enthalpy, but to attain conditions compatible with the double-column process itself.

There are thus two basic causes which necessitate the compression of

air and hence the expenditure of work: the particular process chosen to effect the separation, and the need for refrigeration to offset heat losses.

These two causes are not directly connected, and it is therefore natural to think of dividing the work required to produce oxygen and nitrogen into two parts and to consider it as being expended in two separate operations: compression of air to process pressure and compression of air in a refrigerating cycle. It is evident that the refrigeration needed to offset the heat losses could in principle be supplied from some other source and not from the compression of the air that is to be separated. It is merely a matter of convenience that air is chosen as the refrigerating agent and that this air is the same air as that being separated.

Now a glance at the (T, s) diagram of air on Fig. 86 shows that the curves of constant enthalpy become much steeper as the pressure is increased. Thus compression at a constant temperature of 17° C. from 1 to 10 atm. leads to a decrease in enthalpy of about 1 kcal./kg., while compression at the same temperature from 10 to 100 atm. lowers the enthalpy by about 4 kcal./kg. Yet the work required to compress air from 10 to 100 atm. is about the same as that needed to bring the pressure from 1 to 10 atm. This means that the same amount of refrigeration can be produced by compressing a certain amount of air from 1 to 100 atm. as by compressing five times this amount from 1 to 10 atm. while in the former case the power is only about two-fifths of that consumed in the latter case.

This consideration has led to a change in the original process, according to which the bulk of the air to be separated is compressed only to the 'process pressure' of 5–6 atm., while a comparatively small portion is brought to a very much higher pressure, generally 150–200 atm., for the purpose of reducing its enthalpy and supplying refrigeration. Fig. 109 shows in a schematic flow diagram how this is done. It is evident from this figure that the plant now has two cycles instead of one, a 'process cycle' and a 'refrigeration cycle'. It can also be seen that only the air from the refrigeration cycle traverses the coil in the sump of the lower column. The 'process' air, after being cooled in the exchanger to its dew-point, is admitted at the bottom of the lower column as a saturated vapour.

The 'refrigeration' of this type of air-separating plant differs in no way from an ordinary air-liquefaction cycle, as these were described in Chapter V. The same considerations hold regarding the reduction that

can be achieved in overall power consumption by using customary refrigerants for precooling the compressed air. In large-scale air separation plants it has been found economical to add an ammonia cycle, which increases the refrigerating performance and thus reduces the refrigeration cycle.

Fig. 110 shows a schematic flow diagram of a Linde plant embodying an ammonia cycle and a high-pressure cycle. The compressors and the units for scrubbing out CO_2 from the compressed air are not shown. It

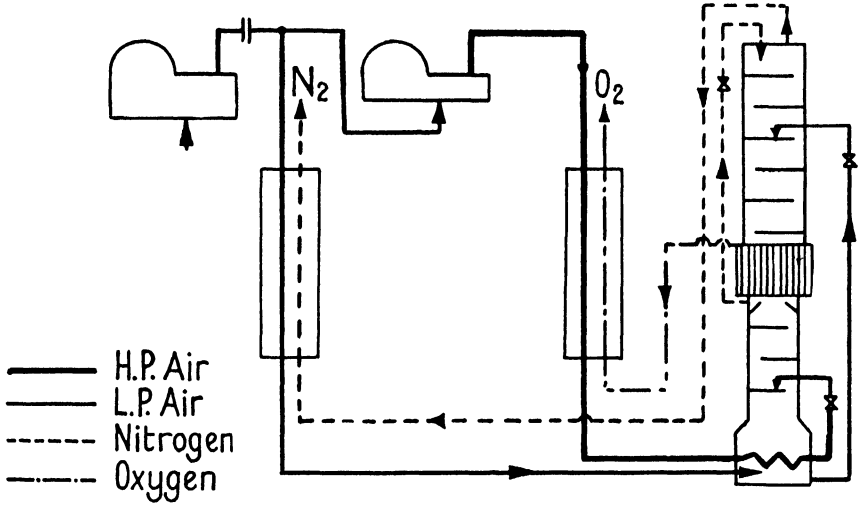


FIG. 109. Linde double air column with high pressure cycle

will be noted that most of the heat-exchangers are duplicated to allow ice to deposit in one period and to be thawed off in the consecutive period of operation. There are two pairs of heat exchangers E_1 and E'_1 before the ammonia cooler, E_1 for the low-pressure air and E'_1 for the high-pressure air. The former is cooled with nitrogen, the latter with oxygen. Similarly, we have two ammonia heat-exchangers, E_2 and E'_2. The former, traversed by low-pressure air, is double; the latter, traversed by high-pressure air, is a single exchanger of helical form. The heat-exchanger E cools only the high-pressure air with the help of oxygen vapour. The larger low-pressure current traverses two tubular heat-exchangers E_3 and E_4, which are cooled with nitrogen. By giving E_3 two parallel sections, the last traces of moisture can be removed and the plant can be made to function for eight months without stopping. Apart from the fact that most of the air enters the lower column as a

vapour from below, the actual separation process is the same as in the previous types.

The Linde double column with low- and high-pressure cycles and ammonia refrigeration is used for large units. It may therefore be of interest to give some details concerning one of them. Some years ago the Linde Co. built a series of large plants to produce pure nitrogen for

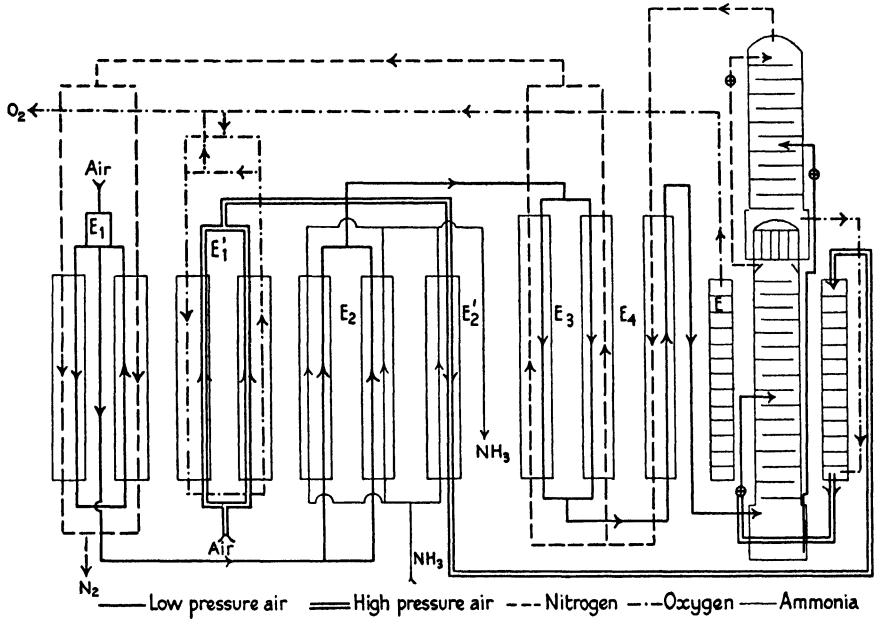


FIG. 110. Linde double air column with high-pressure and ammonia cycles

the synthetic ammonia industry. The purity of the nitrogen was 99·96 per cent., the oxygen leaving the plant was only 94 per cent. and was not further used. The double column was 31½ ft. high. The lower column contained 24 plates, 3 ft. in diameter; the upper column had 35 plates with a diameter of 3 ft. 5 in. The main condenser-evaporator consisted of 6,973 tubes, each about ¼ in. in diameter and 4 ft. 2 in. long. 230,000 cu. ft. of air were separated per hour; of these 49,400 were compressed to 120 atm., the rest to 5 atm. The plant gave 176,500 cu. ft. of pure nitrogen per hour. The power consumption was divided between the various cycles in the following manner:

	$kWh/m.^3$ O_2
Compression of all the air from 1 to 5·7 atm. abs.	0·450
Compression of 17 per cent. from 5·7 to 120 atm.	0·135
Compression of ammonia	0·035
Total power consumption	0·620

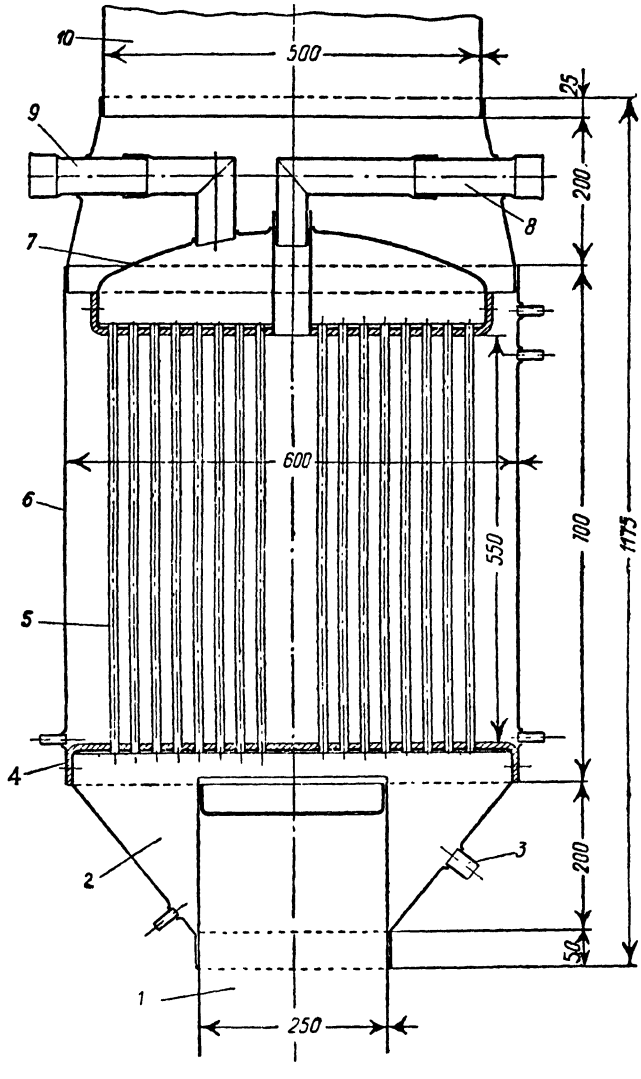


FIG. 112. Condenser-evaporator
(dimensions in mm.)

1. Lower (pressure) column
2. Trough for liquid nitrogen
3. Outlet for liquid nitrogen
4. Tube plate
5. Tubes of condenser
6. Casing of condenser-evaporator
7. Dome
8. Outlet tube for gaseous oxygen
9. Connecting tube to safety valve
10. Upper column (low pressure)

Fig. 111 is a photograph of the condenser-evaporator of a large nitrogen plant. A drawing of a similar condenser-evaporator is shown

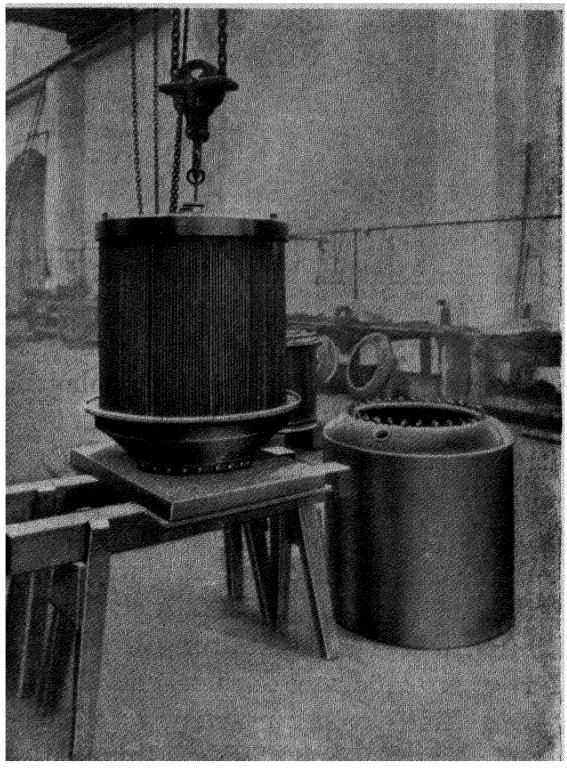


FIG. 111. Condenser-evaporator.
Height about 2 ft. 6 in.

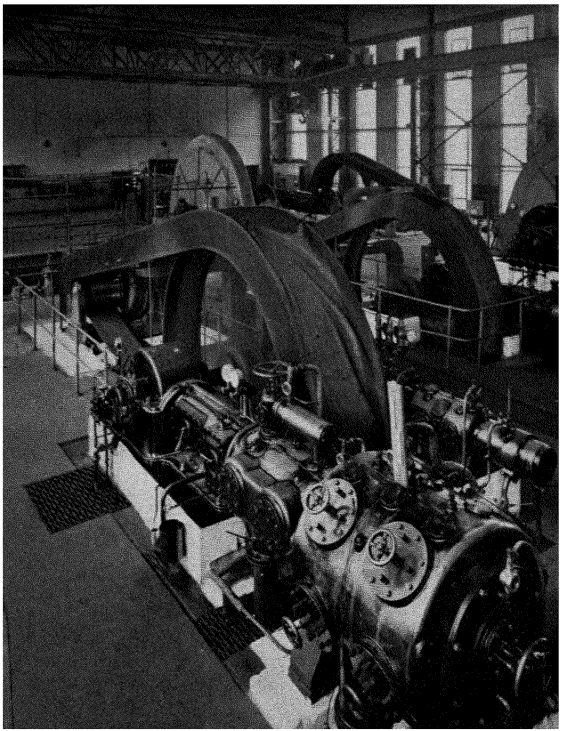


FIG. 113. Air compressor on Linde nitrogen plant

(Reproduced by permission of Messrs. Nitrogen Fertilisers, Ltd., Flixborough)

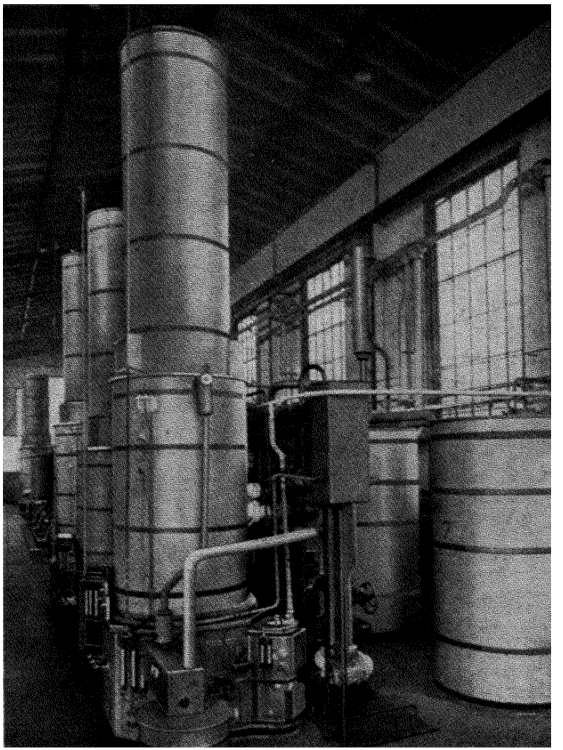


FIG. 114. Plant for producing nitrogen for synthetic ammonia. Height of columns about 16 ft.

in Fig. 112. Fig. 113 shows a large air compressor working on a nitrogen plant. Fig. 114 shows a group of nitrogen units in a German factory.

2. The use of expansion engines and turbines

All the preceding considerations have been based on the assumption that the only means of supplying refrigeration is to lower the enthalpy of the whole or a part of the incoming air. This is correct as long as no other terms occur in the heat balance besides the enthalpy of incoming air and outgoing products and the heat ingress from outside. The assumption ceases to hold as soon as the compressed air or its products do external work. It was shown in Chapter V how this principle was utilized in the Claude and Heylandt air-liquefiers to increase the refrigerating performance by the use of reciprocating expansion engines, and the same device has found wide application in air separation, first in France, later in Germany, and more recently in Russia and the United States.

Expansion engines are particularly useful in the production of liquid oxygen, where a much higher refrigeration load is imposed than when all products leave the plant as gases close to atmospheric temperature. Whereas the theoretical work of separating air into oxygen and nitrogen was shown on p. 149 to be 0·067 kWh/cu. m. of pure oxygen, the minimum work needed in theory to produce the equivalent of 1 m.^{3} as a liquid is 0·234 kWh, i.e. 3½ times as great. The most efficient Claude and Heylandt plants consume about 1·1 kWh/kg. or 1·5 kWh/equivalent cu. m. of liquid oxygen.

Expansion engines have also been employed very successfully in small-scale gaseous plants and are favoured to-day for all mobile units. They lead to a very compact arrangement and, as a result of their high refrigerating capacity, the plants can be started up and run in quickly. The mobile plants built by Clark Bros. in America during the war for use under conditions where no cooling water is available use a two-cylinder expansion engine running at 350 r.p.m. during the starting-up period and 150 r.p.m. in the stationary state.

The **Heylandt liquid-oxygen plant** is shown in diagram in Fig. 115. The working pressure is 200 atm. The compressed air is conveyed directly from the compressor, after purification from carbon dioxide, to the upper section of the heat-exchanger E, where part of the moisture is condensed and withdrawn. The compressed air is finally dried in a caustic-soda battery, after which it divides: 40 per cent. is passed straight

through the lower section of E to the valve V and there expanded to about 5 atm., in the course of which part of it is liquefied. The remaining 60 per cent. is expanded in the cylinder of the expansion engine X to the same pressure, and is thereby cooled to about $-135°$ C. The

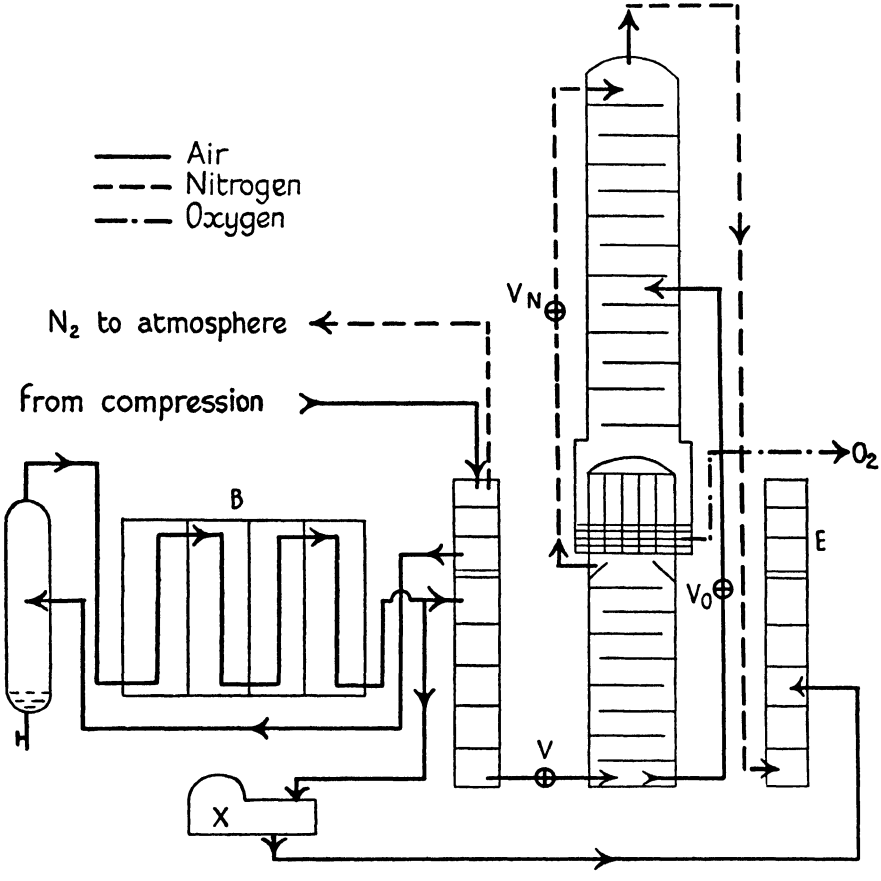


FIG. 115. Heylandt liquid-oxygen plant

expanded cold air re-enters the heat-exchanger at the point where the compressed air is at this temperature, and is cooled further in separate tubes along with the latter. The double column itself is exactly the same as those formerly described, except that there is no coil in the evaporator. All the air, partly liquid and partly vapour, is delivered at the bottom of the lower column. The vapour rises to the summit, while the liquid is transferred through the 'rich air valve' V_0 to the middle of the upper column, as in the Linde plants. The liquid oxygen

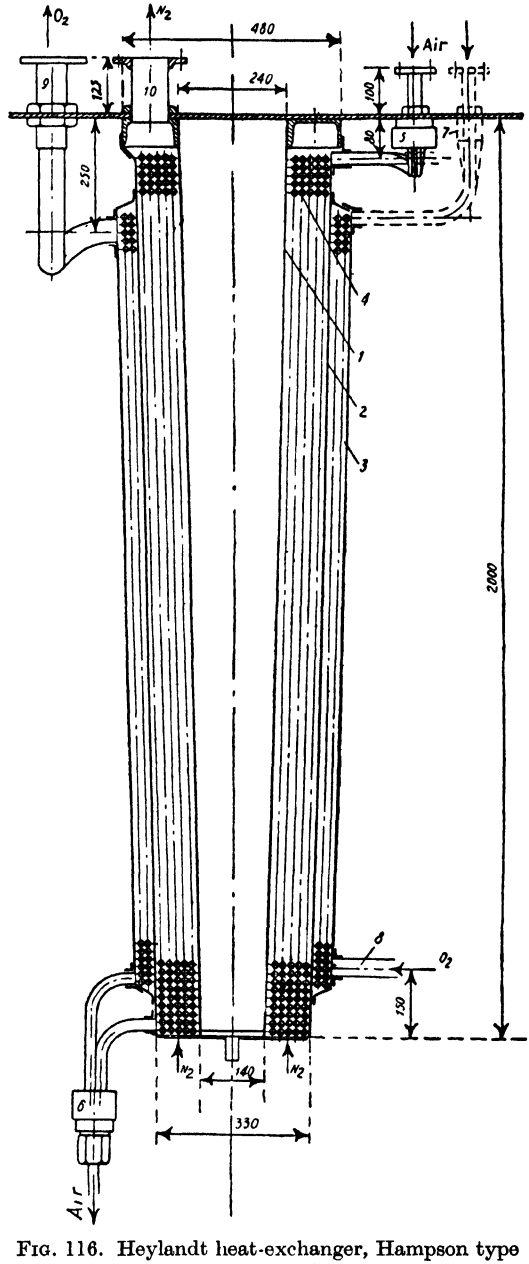


FIG. 116. Heylandt heat-exchanger, Hampson type (dimensions in mm.)

1. Inner jacket
2. Intermediate jacket
3. Outer jacket
4. High-pressure tubing
5. Air inlet
6. Air outlet
7. Air inlet (outer section)
8. Oxygen inlet
9. Oxygen outlet
10. Nitrogen outlet

is withdrawn from the shell of the condenser-evaporator. The plant can also be made to supply liquid nitrogen, which is withdrawn from the trough at the top of the lower column. If gaseous oxygen only is required, the expansion engine can be turned off completely and the pressure lowered to about 60 atm.

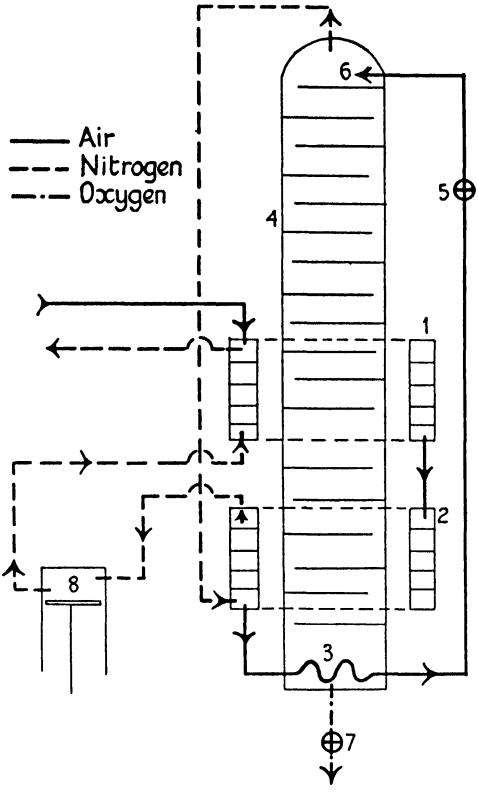


FIG. 117. Le Rouget plant for liquid oxygen

The main heat-exchanger in the Heylandt plants is of the Hampson type and is mounted on the top of the column. Coils of narrow high-pressure tubing are wound horizontally in funnel-shaped jackets, through which the low-pressure gases are passed. The exchanger, a drawing of which is given in Fig. 116, consists of two concentric sections, which are cooled with nitrogen and oxygen respectively.

The simplest 'Air Liquide' unit is the so-called **Le Rouget plant** for small-scale liquid oxygen manufacture, the characteristic feature of which is an expansion engine on the return line of impure nitrogen (see Fig. 117). Air, compressed to 200 atm. and suitably purified, traverses

the two heat-exchangers 1 and 2 in series, whence it passes through the coil 3 in the single column 4. It is then expanded to 4 atm. in the valve 5 and delivered, mostly in the liquid state, at the top of the column at 6. Pure liquid oxygen is withdrawn through the valve 7. Impure gaseous

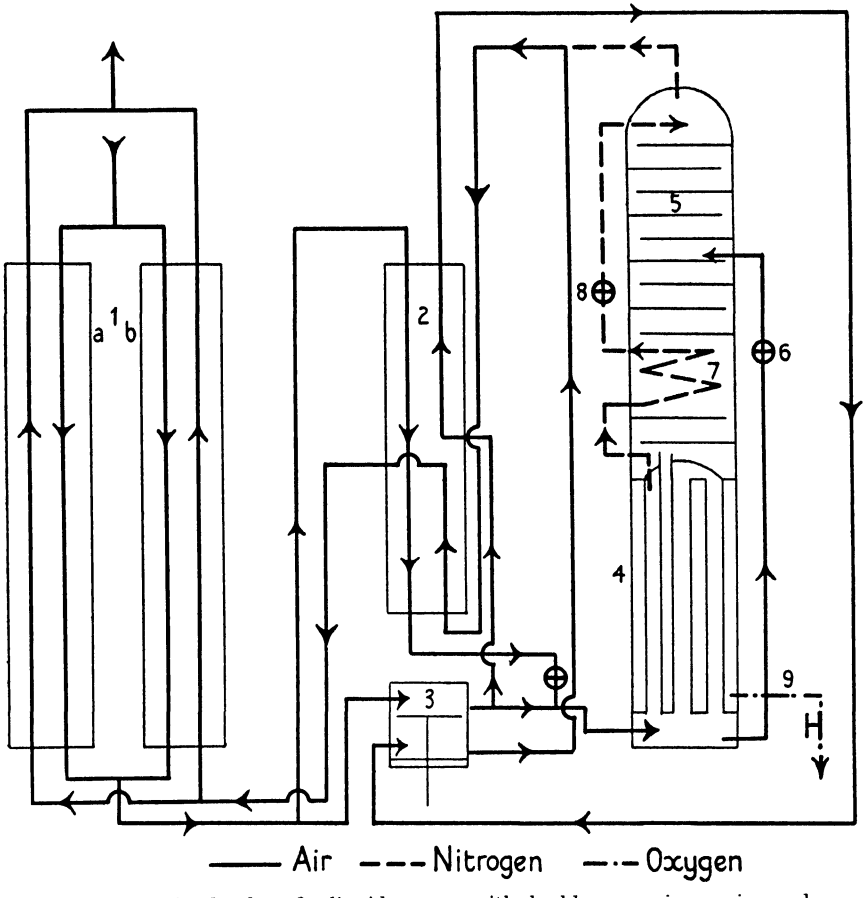


FIG. 118. Claude plant for liquid oxygen with double expansion engine and dephlegmator

nitrogen is passed through the heat-exchanger 2, in which it is warmed up to $-60°$ C., and is then again cooled in the expansion engine 8, in which its pressure is reduced from 4 to 1 atm. It is then brought up to room-temperature in the heat-exchanger 1 and emitted to the atmosphere.

From previous discussions it is apparent that this unit cannot be very efficient. The working pressure is 200 atm. and much oxygen is wasted. Yet it is comparatively simple and useful for small-scale production.

The **large-scale liquid oxygen plant** of 'Air Liquide' (Fig. 118) is

characterized by a dephlegmator and double expansion engine. After passing through the preliminary heat-exchanger 1*a* or 1*b*, at 60 atm. pressure, part of the air traverses the 'liquefier' 2 from top to bottom and is admitted to the base of the dephlegmator after expansion to 4 atm. The rest is expanded, likewise to 4 atm., in the first stage of the expansion engine 3, after which it again separates into two portions. One is added to the partially liquid air behind the valve; the other is warmed by passing up the upper part of 2, and is then expanded to 1 atm. in the second stage of the engine. The expanded air thereupon mixes with the cold nitrogen vapour emerging from the top of the column, and returns through the lower part of 2 and through 1*a* or 1*b*. The oxygen in this air is wasted.

The refrigerant between the tubes of the dephlegmator is liquid oxygen from the column, part of which is withdrawn through the tube 9. The liquid mixture from the sump is expanded to 1 atm. in the valve 6 and admitted in the middle of the column. The nitrogen vapour escaping from the summit of the dephlegmator is liquefied in a coil 7 inside the column by means of liquid reflux, expanded in the valve 8, and thereupon delivered at the top of the column.

3. Large-scale oxygen production

(*a*) *The Linde–Fränkl process*

The plants described in the preceding sections served mainly to produce oxygen for cutting and welding and nitrogen for the synthetic ammonia industry. The quantities of oxygen used for oxy-acetylene work in the engineering industry did not justify the erection of very large plants, and the oxygen was not required to be very cheap as it was in competition mainly with expensive electric energy.

Rather larger amounts of nitrogen were needed and it was mainly in connexion with this product that the Linde Co. developed the separate high- and low-pressure cycles described in § 1. The simultaneous utilization of both products occurred only occasionally for two reasons. The two industries requiring oxygen and nitrogen were seldom combined in one concern, and secondly each industry demanded very pure products and it is not easy to supply simultaneously oxygen-free nitrogen and nitrogen-free oxygen. It was only towards the end of the 1930's that this became economically possible.

Simultaneously with these developments a considerable amount of research and pilot plant work was carried out in Germany, Russia, and the U.S.A. on the use of oxygen in the steel and chemical industries and

for gasification. It was apparent that the prospects were favourable, but only if oxygen became very much cheaper than hitherto. At the same time, it became practically possible to lower the price of oxygen owing to the higher plant capacities that would be required in these fields and because high purity was not essential. Under these circumstances it became very important to reduce the power consumption. This could be achieved in two ways: by increasing the efficiency of the main low-pressure cycle, and by improving the high-pressure refrigeration cycle. Attempts were made in both directions.

It was shown in § 1 that the necessity of compressing the whole of the air to approximately 5·5 atm. is inherent in the double-column process. A closer temperature approach on the two sides of the condenser-evaporator and a reduction in the resistance of the column and exchanger can lead to a slight lowering of this pressure, but since the power consumption is roughly proportional to the log of the compression ratio, it is not easy to save an appreciable amount of power in this way. It is, however, possible to make use of the pressure difference between the two columns to gain additional refrigeration, and the Linde Co. achieved this by introducing a low-pressure expansion engine and later an expansion turbine working at low temperature between 5·5 and 1·5 atm. The power regained in this machine was hardly significant, but the cold so produced was enough to cover most of the refrigeration requirements. By expanding a certain amount of nitrogen, it became possible to reduce the amount of air passing through the high-pressure cycle from 17 per cent. to about 6 per cent. of the total quantity of air treated. This meant that the power consumed by the high-pressure cycle and the ammonia machine could be reduced, theoretically by two-thirds, in practice by about one-half.

Though its effect on the power consumption was less marked, the replacement of the main heat-exchanger by two pairs of alternating regenerators was a still more important innovation. The regenerators had been patented by Fränkl† in 1925, but they were not used successfully for air separation till after 1930.

The advantages offered by regenerators were discussed in Chapter III, as well as some of the conditions governing their use. It was mentioned that pure products are difficult to obtain, since they have to purge the regenerators of mixture at the beginning of the cold period. It is generally found economical to produce oxygen up to 98 per cent. purity in regenerator plant, but in some modern units the purity is raised by

† British Patent, 335,257.

expelling a small portion at the beginning of the period at the cost of a slightly reduced yield.

In the Linde–Fränkl plants the low-pressure air is compressed to 5·5 atm. abs. but the efficiency of compression is somewhat higher than in the earlier plants as the reciprocating air-compressors are replaced by turbo-compressors. The power consumption for units producing between 1,750 and 3,350 m.³ of 98 per cent. oxygen per hour is about 0·55 kWh/cu. m. The following table illustrates the distribution of running costs in a group of three Linde–Fränkl plants together treating 40,000 cu. m. of air per hour and a two-cycle nitrogen plant, as described in the previous section, with a throughput of 6,500 cu. m. of air per hour.

TABLE 19. *Distribution of Running Costs*

	2-cycle Linde plant	*Group of three Linde–Fränkl plants*
Throughput	6,500 m.³/hr.	40,000 m.³/hr.
Power	33%	58·8%
Labour	15	4·9
Chemicals	4·5	0·3
Oil and water	5·5	4·6
Depreciation and maintenance	42	31·4
	100·0	100·0

Fig. 119 shows schematically a typical Linde–Fränkl plant as used in Germany during the last war for producing 3,500 m.³ of 98 per cent. oxygen per hour. 20,000 m.³ of air are filtered and compressed to 5·5 atm. in a turbo-compressor. After traversing an after-cooler and a water-separator, the air is divided into two streams. 19,200 m.³ pass alternately in parallel through two of a group of 4 regenerators which are cooled in the alternate periods by returning cold oxygen and nitrogen. This air is introduced at the bottom of the lower column as a saturated vapour. The remaining 800 m.³ traverse a scrubber for removal of CO_2 and are then compressed to 125 atm. Thereupon the high-pressure air is cooled in 4 successive heat-exchangers, expanded to 5 atm. and introduced into the lower column. The arrangement of the 4 exchangers, known respectively as the precooler, the ammonia-exchanger, the main-exchanger and the turbine-exchanger, is of some importance, as will be described presently. Some gaseous nitrogen is withdrawn from the top of the main condenser-evaporator and a part of this nitrogen is heated in the 'turbine exchanger' cooling the incoming high-pressure air. It is then expanded in the turbine and a part of the expanded nitrogen

joins the main nitrogen stream and returns with it through the nitrogen regenerators. The rest of the expanded nitrogen, 150 m.^{3} in all, returns through the 'main-exchanger' and the 'precooler', giving up its cold to the high-pressure air. In the ammonia-exchanger, between the main-exchanger and the precooler, the high-pressure air is cooled with evaporating liquid ammonia from a small auxiliary ammonia cycle.

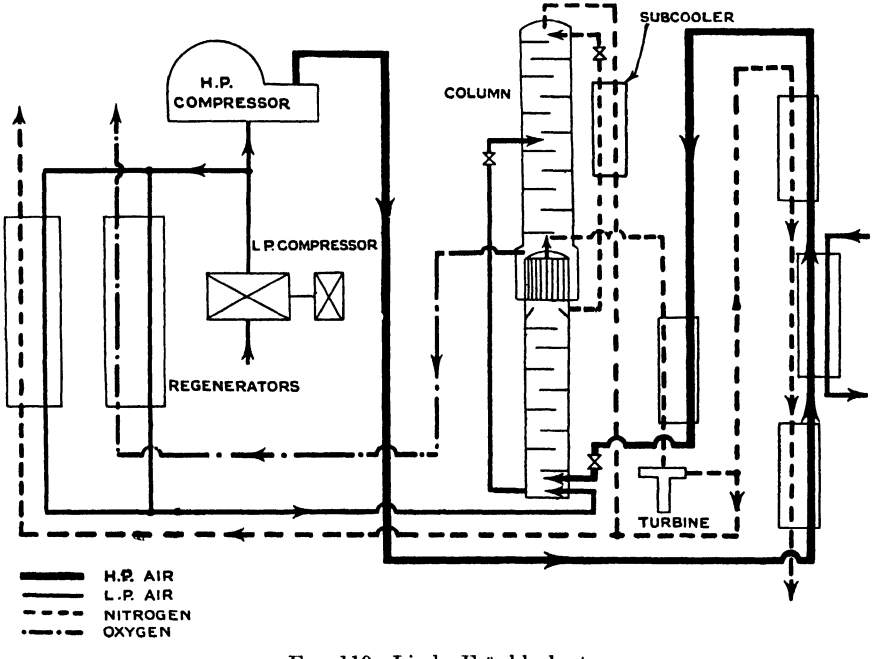


FIG. 119. Linde–Fränkl plant

The ammonia-exchanger and the main-exchanger are duplicated so that one unit can be thawed out while the other is running.

From the main condenser-evaporator liquid oxygen passes into the tubes of an external condenser, not shown in the figure, where it is evaporated, with nitrogen condensing in the shell. This nitrogen is a part of the stream coming from the top of the main condenser, that part, mentioned above, which does not go to the expansion turbine. A small portion of liquid oxygen, which does not evaporate in the external condenser, passes to an acetylene separator and is thence rejected to atmosphere. This arrangement serves the purpose of preventing any accumulation in the plant of acetylene contained in the air, which might otherwise lead to explosions.

The whole of the condensed nitrogen, including that portion which

is formed in the external condenser, is subcooled with low-pressure nitrogen product, before it passes through the expansion valve to the top of the upper column. The nitrogen product, preheated in the liquid nitrogen subcooler, returns through the nitrogen regenerators while the oxygen passes to the oxygen regenerators directly from the outlet at the bottom of the upper column.

The Linde–Fränkl plants are remarkable for the delicate balance of the three combining cycles, which was achieved as a result of a number of alterations that considerably changed the initial layout. Stolper† has recently published a careful analysis of the process and most of the following remarks are based on his paper.

The refrigerating performance of the high-pressure cycle comes partly from the reduction in enthalpy of the air due to compression and partly from the transmission of ammonia refrigeration. The latter is very much cheaper than the former and it is therefore important to absorb as much refrigeration as possible from the ammonia cycle. The ammonia refrigeration is increased by reducing the amount of nitrogen returning in countercurrent with the ingoing high-pressure air. In the plant described above, 800 m.^{3} of high-pressure air are used, and only 150 m.^{3} of expanded nitrogen return through the main exchanger and precooler. By taking the balance of the precooler and the ammonia-exchanger, it can be shown that in addition to the amount of cold that would be taken from the ammonia cycle if the amount of revert gas were the same as that of the incoming air, a further amount is withdrawn equal to

$$\Delta Q = (T_1 - T_2)\,\Delta M\, C_p,$$

where T_1 and T_2 are respectively the temperature of air entering the precooler and leaving the ammonia-exchanger, C_p is the specific heat of the revert gas and ΔM is the difference between the amount of high-pressure air and low-pressure gas. This additional refrigeration is thus proportional to the difference between the amount of incoming air and the amount of outgoing nitrogen in countercurrent with it.

It is not possible to reduce the revert nitrogen beyond a certain limit, as this would result in too high a temperature of the high-pressure air in front of the expansion valve. If no revert gas at all were passed in countercurrent with this air, the temperature of the air in front of the expansion valve would be slightly higher than that of the evaporating ammonia and, in this case, the expanded high-pressure air would be above its dew-point. For the proper functioning of the lower column

† M. B. Stolper, *Kislorod*, **3**, no. 5, p. 18 (1947).

it is not merely necessary for this air to be at its dew-point, but a considerable degree of liquefaction must occur in the valve, resulting in a mixture of liquid and vapour entering the column. It can be shown that the amount of revert gas cannot be less than 18–20 per cent. of the high-pressure air.

That it is possible to reduce the revert gas at all, is due to conditions in the regenerators. An important requirement of the regenerators is that the medium-pressure air shall emerge at its dew-point, and so the heat capacity of the returning products must be adequate to ensure this. Now the specific heat of air at 5·5 atm. is somewhat higher than that of the products at atmospheric pressure and it would appear that it might be insufficient to cool the air to the required temperature. In the older plants, before the introduction of the liquid nitrogen subcooler, the cooling of the air was ensured by the very low temperature of the nitrogen entering the regenerator, 78° K. as against 100° K. for the dew-point of the low-pressure air. But this arrangement had two disadvantages. Firstly the large temperature difference at the cold end of the nitrogen regenerator meant an uneconomic use of low-temperature cold leading to large irreversible entropy increases and a consequent rise in power consumption; secondly, the very cold nitrogen was not able fully to sublime the solid carbon dioxide deposited by the air in the regenerators during the previous period. With the inclusion of the liquid nitrogen sub-cooler, both these difficulties were overcome, but to compensate for the difference in specific heat between the two regenerator streams, it was now necessary to increase the flow of low-pressure products as compared with the ingoing compressed air. But here again the permissible increase is limited. If too much revert gas is passed through the regenerators, it will merely lead to this gas leaving the warm end of the regenerator at too low a temperature, thus nullifying the main advantage of the regenerator, which is a low temperature difference between air and products at the warm end. It must further be noted that the additional nitrogen returning through the regenerator has been deprived of its CO_2 content in the scrubber of the high-pressure cycle and not in the regenerator itself. A larger amount of return gas is thus available to sublime the same amount of CO_2 and this is a further guarantee for the adequate purging of the regenerators.

Finally it may be shown that the expression

$$\Delta Q = (T_1 - T_2)\,\Delta M\, C_p,$$

which was seen to be the additional cold derived from the ammonia by

the inequality of the high-pressure air and product streams, is exactly the amount of cold introduced into the regenerator circuit by the additional nitrogen stream diverted from the high-pressure cycle into the regenerator cycle. It is thus apparent that the gain in refrigeration achieved by the reduction in revert gas through the exchangers is imparted to the plant by diverting a part of the expanded nitrogen from the refrigeration cycle to the regenerators.

In the above example, in which 19,200 m.^{3}/hr. of air traversed the regenerators, 800 m.^{3}/hr. went through the high-pressure cycle and 150 m.^{3} of low-pressure nitrogen were returned through the exchangers, Stolper has calculated the following figures for the various contributions to the refrigeration performance.

Cold obtained from the high-pressure cycle with ammonia refrigeration with equal streams of high-pressure air and revert nitrogen	Q_1 = 17,400 kcal./hr.
Additional cold obtained from ammonia as the result of inequality of the two streams	Q_2 = 15,300 kcal./hr.
Cold obtained by compression of low-pressure air to 5·5 atm.	Q_3 = 5,800 kcal./hr.
Cold obtained from expansion turbine	Q_4 = 26,700 kcal./hr.
Total refrigerating performance	Q = 65,200 kcal./hr.

This shows that the additional cold produced by correctly adjusting the refrigeration stream nearly doubles the performance of the refrigeration cycle and provides 23 per cent. of the total cold requirements of the plant.

Since the total throughput of the plant is 20,000 m.^{3}/hr., this calculation also shows that the refrigerating capacity is 3·25 kcal./m.^{3} of air treated. This is a fairly high figure for so large a plant and it may well be assumed that not the whole of this capacity is utilized during normal running in a stationary state.

(*b*) *The low-pressure cycle*

The distinction between 'process' and 'refrigeration' and the consequent division of the air into a larger low-pressure and a smaller high-pressure stream marked a notable advance in the technique of air separation. It led to a considerable decrease in power consumption and this advantage was particularly significant in large-scale plant. In this way the two-cycle process facilitated the production of large quantities of oxygen and nitrogen. The development of the Linde–Fränkl process, with its use of expansion turbines driven by produced nitrogen, cut right across the conception of one cycle for the rectification process and another to produce the cold. On the one hand the turbine itself, which produced a large portion of the refrigeration requirements, was not, in

fact, a part of the refrigeration cycle; on the other hand the latter cycle was so reduced in size that it appeared as a somewhat anomalous excrescence that might just as well be left out altogether.

It is thus very natural that attempts should have been made to eliminate the high-pressure refrigeration cycle and revert again to a one-cycle plant, by the use of a turbine working close to the process pressure.

In 1939 Kapitza† described an experimental air-liquefaction plant featuring regenerators and a novel type of expansion turbine working at a pressure of 6–7 atm. After passing through one regenerator, the larger portion of the air was expanded in the turbine and rejected after returning through the other regenerator. On its way from the turbine to the regenerator, the air passed through a condenser in which it liquefied the other, smaller portion of the air at 7 atm. This was then expanded in a valve to atmospheric pressure and the flash gas joined the rest of the revert air from the turbine. This principle was followed up in Russia for the production of gaseous and liquid oxygen and several plants were built along these lines during the war, including a large unit producing 2 tons of liquid oxygen per hour. For liquid oxygen production this method has been found to be uneconomical and it was abandoned in Russia after the war in favour of other processes.

The turbine developed by Kapitza differs considerably from those used by the Linde Co. before and during the war. Kapitza drew attention to the fact that air at 7 atm. and very low temperatures is in some respects more similar to water than to steam. Instead of the axial and outward-flow radial impulse turbines introduced by Linde, he developed an inward-flow radial reaction turbine which made use of the high centrifugal forces set up in the dense medium at high speeds of rotation. His experimental model, which passed about 9 m.^{3} of air per minute, was only 8 cm. in diameter and ran at a speed of 42,000 r.p.m. Whereas the efficiency of the Linde turbines was only 55–60 per cent., Kapitza's turbine was reported to approach 80 per cent. efficiency. Similar turbines were designed by Swearingen‡ for the Kellogg Co. in America and efficiencies slightly above 80 per cent. were claimed. Table 20 gives the characteristics of air expansion turbines that have been described in the literature.

In the Linde–Fränkl plant, as described previously, the turbine is fed with nitrogen withdrawn from the condenser at the top of the lower column, and the cold which it produces is transmitted to the air of the

† P. L. Kapitza, *Journ. of Phys. U.S.S.R.* **1**, 7 (1939).

‡ J. S. N. Swearingen, *Trans. Amer. Inst. Chem. Eng.* **43**, no. 2, p. 85 (1947).

TABLE 20. *Characteristics of Air Expansion Turbines*

Origin	*Date*	*Type*	*Throughput* $m.^3/hr.$	*Speed* *r.p.m.*	*Tip Velocity* *m./sec.*	*ft./sec.*	*Diameter* *cm.*	*Reference*
Linde Co., Germany	1937	Impulse	4,500	7,000	115	377	30	(1) (2)
Bolshevik Works, Russia	1939	Impulse	5,900	7,000	132	433	36	(1)
Kapitza, Russia	1940	Reaction	550	42,000	175	570	8	(3)
Kellogg Co., U.S.A.	1944	Reaction	2,500	22,000	200	660	17·5	(2)

(1) S. Y. Gersh, *Obogaschenny Vozdukh*, Moscow, 1939, pp. 89–96.
(2) J. S. N. Swearingen, loc. cit.
(3) P. L. Kapitza, *Journal of Physics, U.S.S.R.* **1**, 7 (1939).

high-pressure circuit. The maximum amount of nitrogen that can thus be withdrawn without disturbing the rectification process is between 10 and 20 per cent. of the total amount treated.

In the Russian and American low-pressure plants, the turbine is fed with compressed air, a portion of which is diverted behind the regenerators, warmed up in a heat-exchanger and fed through the turbine into the middle of the upper column. The passage of gaseous air direct to the upper column at atmospheric pressure is known as the Lachmann principle. It lowers the reflux ratio and reduces the irreversibility of the upper column. Just over 20 per cent. of the total amount of air treated can take this path without overstepping the minimum reflux ratio.

The total available heat drop for the isentropic expansion of air from 6 to 1·2 atm. if the end of the expansion corresponds to saturated vapour, is 13 kcal./$m.^3$ With an efficiency of 80 per cent., one cu. m. of air will therefore deliver 10·4 kcal. For a large plant, the total refrigerating requirements are about 2·5–3 kcal./cu. m. of air treated or 12·5–15 kcal./$m.^3$ of oxygen produced. Of these about 2 kcal. are obtained by compression of the gas to 6 atm. and subsequent isenthalpic expansion, leaving 10·5–13 kcal. to be delivered by the turbine. For every cu. m. of oxygen made, it is therefore necessary to pass about 1–1·25 cu. m. of air through the turbine, or about 19–24 per cent. of the air treated. This is about the maximum amount of air that can be diverted to the upper column.

Fig. 120 shows a plant proposed by the Kellogg Co. in America according to the Low-Pressure Process. The air is compressed to $6\frac{1}{4}$ atm. and cooled in reversing heat-exchangers of a novel type to be described presently. The major portion of the air, leaving the exchangers at its

dew-point, is introduced as a vapour at the bottom of the lower column. A smaller portion is slightly heated and fed through the turbine into the middle of the upper column at 1·4 atm. The return nitrogen stream subcools first the liquid nitrogen from the top and then the enriched mixture from the bottom of the lower column. After passing a further heat-exchanger (not shown) it returns through the reversing-exchanger.

These reversing-exchangers, first designed by Collins and subsequently

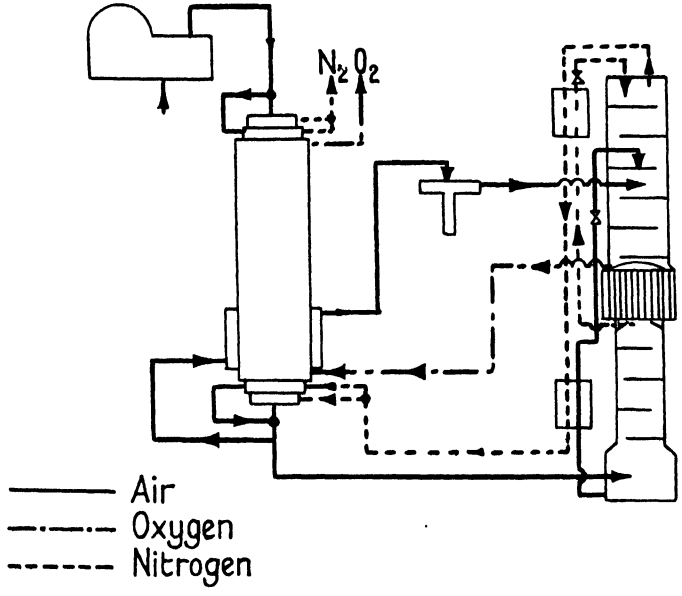


FIG. 120. Kellogg low-pressure plant

developed by Trumpler,† contain a number of packed passages. Oxygen passes continuously through one passage in the same direction, while compressed air and return nitrogen alternate in opposite directions through two other passages. Under these conditions the temperature difference in the lower part of the exchangers would be too great to ensure the complete sublimation of all the ice and CO_2, which is deposited on the walls in the same way as in the case of regenerators. To meet this difficulty, a small portion of the cold air, the so-called unbalance stream, is diverted and returned through a further passage in countercurrent with the main compressed air, thus serving to reduce the temperature difference between compressed air and returning nitrogen sufficiently to enable the exchanger to be purged completely. This unbalance stream, which naturally emerges from the alternating

† P. R. Trumpler and B. F. Dodge, *Chem. Eng. Progr.* i, no. 2, p. 75 (1947).

exchanger at a higher temperature than the main stream, is cooled in the exchanger in countercurrent with the returning nitrogen and blended with the stream that feeds the turbine, thus raising the temperature of this stream sufficiently to prevent condensation in the turbine itself. Alternatively the 'unbalance stream' can be a part of the returning nitrogen, which thus passes twice through the lower portion of the exchanger.

The most obvious advantage of the reversing-exchangers is that they enable pure oxygen to be produced without a highly complex switchgear,

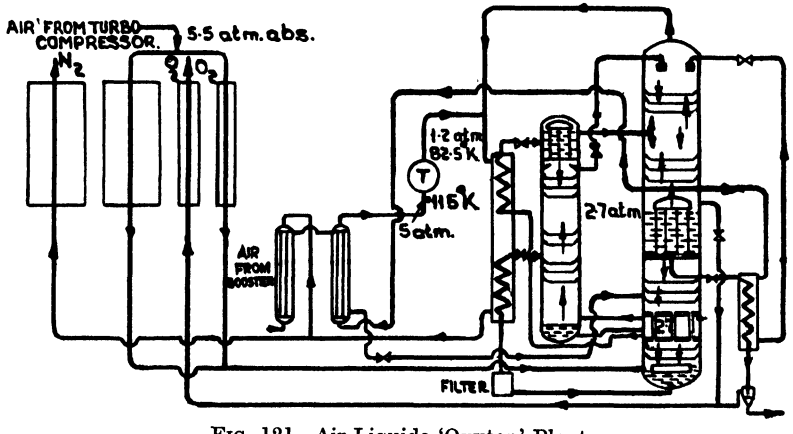


FIG. 121. Air Liquide 'Oxyton' Plant

and without loss of yield. Since the oxygen passes continuously through the same passage, it is never contaminated with CO_2 and nitrogen. With the 'unbalance stream' the exchangers further allow complete purging in a way that would be impossible with the use of regenerators alone without further modifications. In the Linde–Fränkl plants, as mentioned above, the purging was ensured by the introduction of the nitrogen from the high-pressure circuit, from which the CO_2 had been removed by chemical means. With the elimination of the high-pressure circuit, this additional purging stream disappears also and other means must be found of securing the complete sublimation of the CO_2. The Collins exchanger solves this problem and it is therefore an important contribution to the success of the Low-Pressure Process which is now competing with the Linde–Fränkl plant in the field of large-scale oxygen production.

A further low-pressure plant for capacities between 5,000 and 15,000 cu. m. of oxygen per hour has been developed by the Air Liquide Company in France. This so-called 'Oxyton' plant,† a schematic flow

† T. Bishop, *The Iron and Coal Trades Review*, 9 Apr. 1948.

diagram of which is shown in Fig. 121, uses regenerators and expansion turbines in an arrangement somewhat similar to the Linde–Fränkl plant, but rectification is effected in three columns, working at 5–6, 2·5–3, and 1·2 atm. abs. respectively. This feature reduces the irreversibility of the rectification process and thus lowers the power consumption. The regenerators are balanced by a stream containing only 3 per cent. of the total air treated, which is compressed to 10 atm. in a booster, deposits ice and CO_2 in one of two alternating exchangers, is cooled and liquefied in further exchangers and admitted to the high-pressure column.

At the time of writing, a new plant which has been developed by the British Oxygen Co. in England is not yet on the market. This so-called 'Rescol' plant features regenerators and a single column, complete separation of the air being secured by re-compressing and re-liquefying a part of the produced nitrogen to supply the necessary reflux.†

† M. Schuftan, *Proc. Inst. Chem. Eng.* (in the press).

VIII

EFFECT AND EFFICIENCY OF PLATE COLUMNS

1. The effect of plates with mixed liquid

In Chapter VI it was shown how, under certain simplifying assumptions, the number of plates theoretically required in a rectifying column, in order to produce a specified degree of separation, could be computed. The calculations were carried out on the (h, x) diagram with the help of the concept of *equivalent currents*. The advantage of the (h, x) diagram was that it enabled us to determine simultaneously the quantity of heat transferred at various points of the plant.

In engineering practice it is often found expedient to consider the changes in concentration, brought about on the plates of a column, without at the same time taking the heat transfer into account. For this purpose it is useful to employ a chart that is rather simpler than the (h, x) diagram. The *composition diagram*, in which the composition of the vapour is plotted as a function of the composition of the liquid, actually gives us less information than the (h, x) diagram; but it is met with so frequently and has been referred to so often in the literature that our presentation would be incomplete if we did not consider it.

If, for the case of oxygen–nitrogen mixtures, we plot the composition z of a vapour as a function of the composition x of a liquid with which it is in equilibrium, we obtain the curve shown in the diagram of Fig. 122. If x and z are measured in percentages of nitrogen, the curve is convex towards the ordinate axis, since there is always more nitrogen in the vapour than in the corresponding liquid.

Now in a certain horizontal section of a rectifying column of the type heretofore described, let y be the nitrogen concentration of a vapour in contact with a liquid containing x per cent. of nitrogen. Since, as we know, this vapour is not in equilibrium with the liquid, it will not be represented by a point on the curve in Fig. 122.

To determine y as a function of x, we must go back to the argument of Chapter VI. Here we showed that, if L and G are the liquid and vapour phases respectively in a certain horizontal section of the column, the equation

$$L - G = F = \text{const.} \tag{1}$$

held throughout the column, provided that no substances were introduced or withdrawn on the way. This equation was to be considered as an abbreviation for the three balance equations of mass, composition,

and enthalpy:

$$\left.\begin{aligned} m_L - m_G &= m_F, \\ m_L x_L - m_G x_G &= m_F x_F, \\ m_L h_L - m_G h_G &= m_F h_F. \end{aligned}\right\} \qquad (2)$$

Using the same arguments, it can be shown that the products $m_L \lambda_x$ and $m_G \lambda_y$ are constant throughout the column, where λ_x and λ_y are the

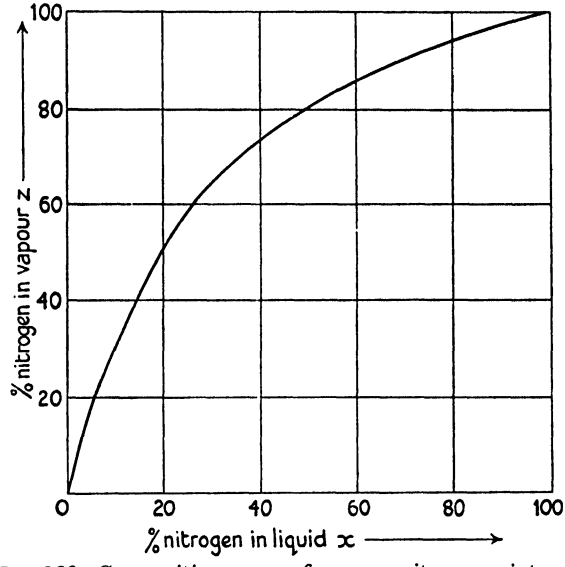


FIG. 122. Composition curve of oxygen–nitrogen mixtures

latent heats of evaporation, at constant pressure and constant composition (see Chapter IV, § 3), of liquids with the compositions x and y respectively.

Since, in an air column, the nitrogen concentration increases towards the top, and since the latent heat of evaporation of nitrogen is slightly less than that of oxygen, it follows that m_G, the amount of vapour passing a horizontal section of the column in a specified time, is greater at the top than at the bottom. But since the latent heats differ but slightly (1,632 cal./mole for oxygen, and 1,337 cal./mole for nitrogen) the change of λ can frequently be neglected. For not too accurate calculations we can thus simply put $m_G = \text{const.}$ and similarly $m_L = \text{const.}$ In this case we can compute the composition of liquid and vapour on any plate as follows with the help of the first two equations of (2).

For any two adjacent plates 1 and 2 these equations give us

$$m_{L_1} - m_{G_1} = m_{L_2} - m_{G_2},$$

$$m_{L_1} x_1 - m_{G_1} y_1 = m_{L_2} x_2 - m_{G_2} y_2,$$

or, since $m_{L_1} = m_{L_2} = m_L$ and $m_{G_1} = m_{G_2} = m_G$,

$$m_L(x_1 - x_2) = m_G(y_1 - y_2);$$

whence

$$y_2 - y_1 = \frac{m_L}{m_G}(x_2 - x_1), \tag{3}$$

or for any point in the column

$$y = \frac{m_L}{m_G}x + y_1 - \frac{m_L}{m_G}x_1, \tag{4}$$

where x_1 and y_1 are the compositions of liquid and vapour at one end of the column.

The composition y of vapour in contact with liquid of composition x is thus given by the points of a straight line. Since $m_G - m_L = m_D$, the amount of overhead product, and since m_L/m_D is the reflux ratio R, the slope m_L/m_G can be expressed in terms of the reflux ratio as $m_L/m_G = R/(R+1)$. If the column ends in a total condenser or evaporator, $y_1 = x_1$, and equation (4) can be written

$$y = \frac{R}{R+1}x + \frac{1}{R+1}x_1. \tag{5}$$

If we write equation (3) in the form

$$\frac{m_L}{m_G} = \frac{y_2 - y_1}{x_2 - x_1} \tag{6}$$

and suppose the suffixes 1 and 2 to refer to the two ends of the column, we can determine the amount of liquid reflux m_L required to produce a specified rectifying effect on a given quantity m_G of gas of known composition.

If we do not neglect the differences of the latent heats, we obtain for two neighbouring plates n and $n+1$

$$m_{G_{n+1}} = m_{G_n}\frac{\lambda_{y_n}}{\lambda_{y_{n+1}}}, \tag{7}$$

and, with the help of equations (2),

$$x_{n+1} = \frac{m_{L_n}x_n + m_{G_{n+1}}y_{n+1} - m_{G_n}y_n}{m_{L_n} + m_{G_{n+1}} - m_{G_n}}. \tag{8}$$

If we put $y_{n+1} = z_n$, i.e. assume complete equilibration on each plate, we can calculate from (7) and (8) the composition of liquid and vapour on each plate successively. Equation (4) follows from (8) if we put $m_{G_{n+1}} = m_{G_n}$, or, which comes to the same thing, $\lambda_{y_n} = \lambda_{y_{n+1}}$.

If we take the differences in latent heats into consideration, the line giving y as a function of x will be slightly curved. For the case

of oxygen–nitrogen mixtures, it is generally assumed to be straight, and is known as the *working line.*

Now suppose the working line $y(x)$ of a column to be known from the specified conditions at the ends, and the curve $z(x)$ to be determined from the equilibrium diagram. Let y_n be the composition of a vapour on entering the nth plate from below, in contact with a liquid x_n leaving the same plate (see Fig. 123). Then the point (x_n, y_n) lies on the working

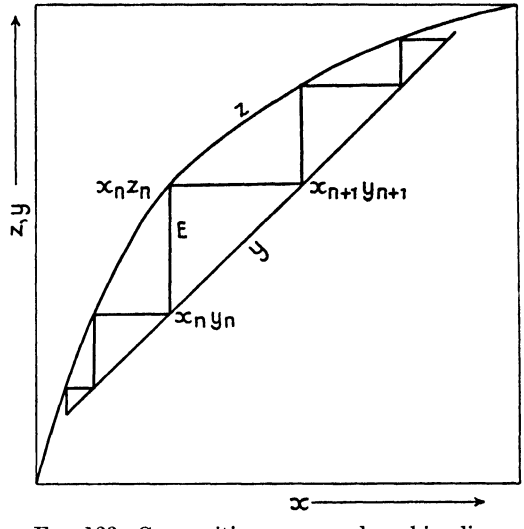


FIG. 123. Composition curve and working line. Method of determining the number of plates

line. On passing through the plate, the vapour will approach equilibrium with the liquid x_n. If equilibrium is actually attained, the vapour will leave the plate n with a composition z_n, the point (x_n, z_n) being on the equilibrium curve. The distance $z_n - y_n$, the *distance from equilibrium* of the vapour on entering the plate, is at the same time the maximum change in composition which the vapour can undergo on passing through the plate. We shall call $z_n - y_n$ the *theoretical effect* E, or simply the *effect* of the nth plate. The ratio of the actual change of composition, undergone by the vapour on passing through the plate, to this maximum change will be termed the *efficiency* ϵ of the plate.

The fact that the effect or maximum change in composition is equal to the distance from equilibrium $z_n - y_n$ on entering is not a general law, but is due to the particular type of plate that we are here discussing, i.e. a plate on which the composition of the liquid is the same at all points. We shall see later that plates may be designed for which

E is considerably greater than $z_n - y_n$. But for the moment we shall keep to plates of the kind already described.

Now if the efficiency ϵ of our plate is equal to unity, the vapour will leave it with a composition z_n and proceed to the $(n+1)$th plate above. Thus $z_n = y_{n+1}$, and (x_{n+1}, y_{n+1}) will again be a point on the working line, and it can be found by drawing a horizontal line from z_n (see Fig. 123). In this way we can draw a series of steps, which will give us the number of plates needed, assuming always that $\epsilon = 1$, and the composition of liquid and vapour on each plate can be determined.† The result will probably not be a whole number of plates, but this cannot be expected. The theoretical number of plates, obtained according to this method, is usually defined as the nearest whole number exceeding the graphical result.

The number of plates obtained will be nearly the same as that resulting from the method described in Chapter VI, but it will be slightly less accurate, as it assumes the constancy of m_G and m_L throughout the column. The principal advantage of this method, as against that used in Chapter VI, is that it is based on the equilibrium curves alone and does not require the knowledge of h.

The next approximation for computing the number of plates required is to assume an efficiency $\epsilon < 1$, which may be taken from past experience, and to suppose that this ϵ is the same for all the plates of the column. In this case, the practical change in composition, undergone by a vapour in passing through the nth plate, will be given by the equation

$$y_{n+1} - y_n = \epsilon(z_n - y_n). \tag{9}$$

The point (x_{n+1}, y_{n+1}) will therefore lie on the working line somewhat lower than (x_{n+1}, z_n). It may thus be connected with (x_n, z_n) by a straight line that is not horizontal, but slopes downwards from left to right, as in Fig. 124. We can show that all these lines in the staircase so obtained have the same slope. Consider two neighbouring plates and the corresponding diagram and draw the two horizontal lines, as shown in the figure. Then the triangles ACD and DFG are similar, since the corresponding sides are all parallel. Therefore

$$AC/DF = CD/FG.$$

But, according to our assumption,

$$AC/AB = DF/DE = \epsilon.$$

Therefore

$$AC/BC = DF/EF;$$

† McCabe and Thiele, *Ind. Eng. Chem.* **17**, 605 (1925).

whence $$AC/DF = BC/EF = CD/FG.$$

Therefore, since the angles at C and F are equal, the triangles BCD and EFG are similar. Therefore, since BC and EF are parallel, it follows that BD is parallel to EG.

If the two ends P and Q of the working line are given, as well as

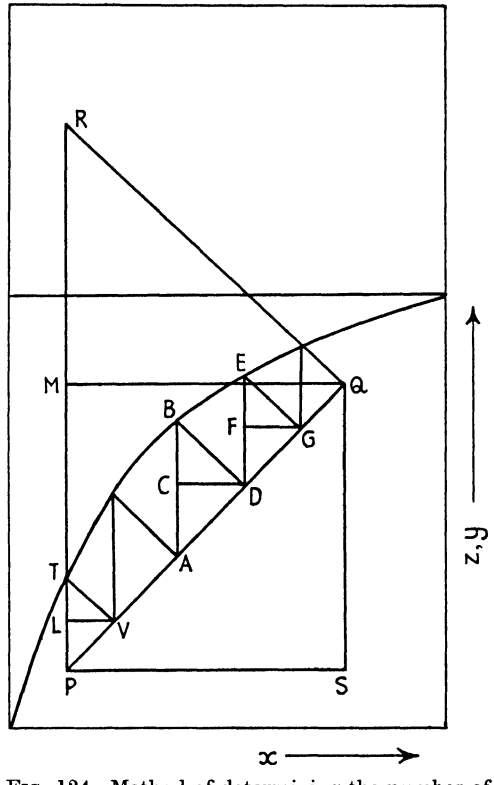


FIG. 124. Method of determining the number of plates for a constant efficiency less than unity

the efficiency ϵ, we can obtain the common slope of all the steps as follows (see Fig. 124): Describe a vertical straight line PR so that $PR = QS/\epsilon$. Then RQ has the slope of the steps. This may be proved as follows: Let TV be the first step, and draw TV parallel to RQ. Then, since the triangles RQP and TVP are similar, and VL is parallel to QM, $$QS/PR = MP/PR = PL/PT = \epsilon.$$

Thus TV has the correct slope of the steps if it is parallel to QR.

The above arguments are valid only for a single column to which mixture is delivered at the top or bottom. If liquid or vapour is introduced or withdrawn at some point in the middle of the column, the

working line will show a break at that point. There will be two working lines, one for the part of the column below the inlet or outlet, and the other for the upper part. The two lines will meet at an angle at this point.

Consider a single column with an evaporator and a condenser, to which liquid is introduced at the middle; and let us suppose, for the sake of convenience, that the column has so many plates that both products are practically pure. Then the lowest point of the lower working line and the highest point of the upper working line will practically coincide with points on the equilibrium curve corresponding to 0 and 100 per cent. respectively. We may now further assume that the liquid entering in the middle is at its boiling-point and is introduced at a point of the column at which the liquid reflux has the same composition as the liquid entering.

With these assumptions it can be shown that the amount of reflux required will be a minimum if the composition of the vapour at the point of entry is such as to be in equilibrium with the liquid entering the column, in which case the two working lines will meet at the equilibrium curve. For, according to equation (6),

$$\frac{m_L}{m_G} = \frac{y_2 - y_0}{x_2 - x_0}, \tag{10}$$

where 0 and 2 refer to the inlet and the top of the column respectively. According to our assumption, $x_2 = y_2 = 1$, so that

$$\frac{m_L}{m_G} = \frac{1 - y_0}{1 - x_0}. \tag{11}$$

Therefore, the greater y_0, the smaller m_L will be. But the maximum value of y_0 is obviously z_0, the composition of a gas in equilibrium with x_0.

A minimum of m_L means a minimum of condensation in the condenser and therefore a minimum of refrigeration at that point. It is therefore economical to condense as little reflux as possible. On the other hand, the diagram here considered entails an infinite number of plates. In practice a compromise will be sought that will keep the required number of plates down to an acceptable figure without unduly increasing the reflux and with it the consumption of energy. This means that (*a*) the products will not be perfectly pure, and (*b*) the vapour at the inlet will contain less of the more volatile component than is in equilibrium with a liquid of the composition x_0.†

† For a more detailed treatment of rectification in plate columns see C. S. Robinson and E. R. Gilliland, *The Elements of Fractional Distillation*, 3rd edition, McGraw-Hill, 1939.

2. Plates with inhomogeneous liquid

Up till now we have assumed that the *effect* of a rectifying plate, i.e. the maximum change in composition, undergone by a vapour on passing through a plate, is equal to the difference in composition $z-y$ between the vapour entering the plate and a vapour in equilibrium with the liquid leaving it. The 'staircase method' of determining the required number of plates, as well as the method discussed in Chapter VI, was based on this assumption, which, until recently, was thought to be universally valid.

Now all the arguments which led us to this view are themselves based on another assumption, which is that the liquid on a plate is homogeneous, i.e. that its composition is the same at all parts of the plate. In plates of older pattern this was always brought about by so designing them that the liquid was violently stirred by the bubbles of vapour passing through it and had itself no definite direction of flow. It was, in fact, more or less tacitly assumed that this arrangement would lead to the greatest effect of a plate, i.e. would produce the greatest change of composition in a vapour passing through it.

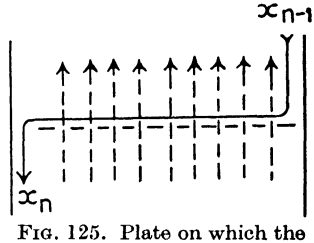


FIG. 125. Plate on which the liquid is not stirred and has a definite direction of flow

Some years ago Hausen† and Kirschbaum‡ showed theoretically that this assumption is untrue, and in modern separating plants a type of plate is employed which has a greater effect than those hitherto described.

Suppose a plate to be so designed that the liquid on it has a definite direction of flow and that the liquid in one part does not mix with that in another part of the plate. Let the composition of the liquid arriving on the plate be x_{n-1}, and that of the liquid leaving x_n (see Fig. 125). The composition of the liquid will change continuously from x_{n-1} to x_n as it passes over the plate. We assume that the plate is perforated in the usual way and that the vapour passes up through the holes as in the older type. Unless particular precautions are taken, the vapour entering the plate from below will also vary in composition from point to point, owing to its past interaction with liquid on lower plates.

Let y_n be the mean composition of the vapour below the plate. Then (x_n, y_n) is a point on the working line, which is defined as before. Now

† H. Hausen, *Forschung auf dem Gebiet des Ingenieurwesens*, **7**, 177 (1936).
‡ E. Kirschbaum, ibid. **5**, 245 (1935); E. Kirschbaum and E. Quade, ibid. **8**, 63 (1937).

since x_n is the composition of the liquid leaving the plate, the mean composition x'_n of the liquid on the plate will be greater† than x_n. Therefore the mean composition z'_n of a vapour in equilibrium with a liquid on the plate will be greater than z_n, the composition of a vapour in equilibrium with x_n. The maximum mean change of composition,

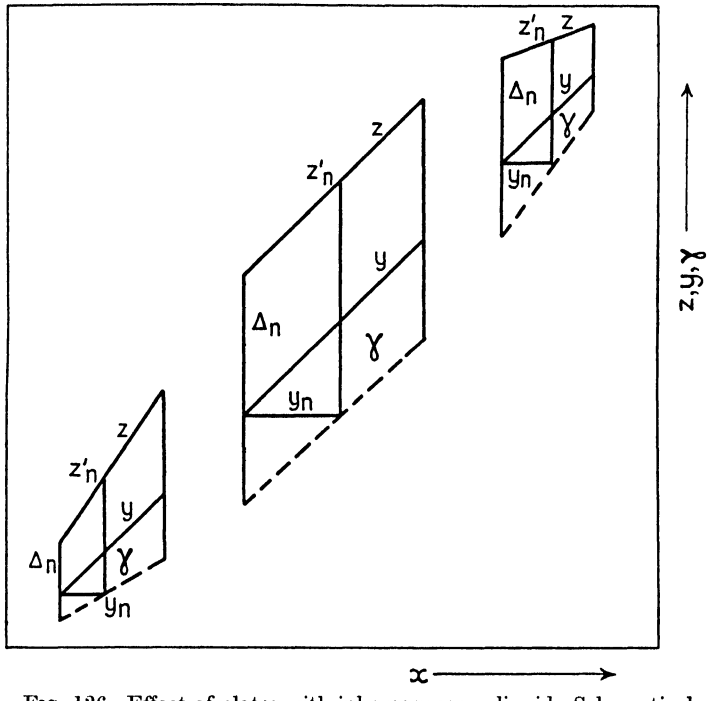


FIG. 126. Effect of plates with inhomogeneous liquid. Schematical portions of equilibrium curve (z), working line (y), and curve giving composition of vapour entering plate from below (γ)

incurred by the vapour in passing through the plate, will now be $z'_n - y_n$, and this is greater than $z_n - y_n$. Now $z'_n - y_n$ is the effect of the plate, as it is the maximum value of $y_{n+1} - y_n$.

To make this clear, consider again the working line in conjunction with the equilibrium curve $z(x)$. The latter, in oxygen–nitrogen mixtures, is very steep at low values of x and becomes flatter as x approaches unity. In Fig. 126 part of the equilibrium curve is shown schematically as a broken line consisting of three parts. The first is steeper than the working line, the second is parallel to it, and the third is flatter.

The steeper the equilibrium curve, as compared with the working

† Greater because we agreed to measure compositions by the concentration of the more volatile component.

line, the greater z'_n will be, as compared with z_n, for a given value of $x'_n > x_n$, and thus the greater will be the effect of the plate.

Now let $b = dz/dx$, the slope of the equilibrium curve at the point x. The slope of the working line is m_L/m_G. If we now put

$$bm_G/m_L = \beta, \tag{12}$$

the effect of the new plate will be the greater, as compared with that of the old plate, the greater β.

Let the effect of the old plate $z_n - y_n = \Delta_n$. (13)

Then, according to Hausen, the expression

$$\phi = \frac{y_{n+1} - y_n}{\Delta_n} \tag{14}$$

is called the *equilibration ratio.* If complete equilibrium is reached between liquid and vapour, i.e. if the efficiency of the plate is equal to unity, $y_{n+1} = z'_n$ and

$$\phi = \frac{\text{effect of new plate}}{\text{effect of old plate}}.$$

In Fig. 126 the dotted line shows the actual composition γ of the vapour, as it varies from place to place. y_n is the mean value of γ for a certain plate. $z - \gamma$ is the effect of a given point on the plate, and $z'_n - y_n$ is the effect of the plate as a whole.

In the lower part of Fig. 126, in which $\beta > 1$, we see that $z - \gamma$ increases with increasing values of x; in the central part, in which $\beta = 1$, $z - \gamma$ is a constant; in the top portion, where $\beta < 1$, $z - \gamma$ decreases as x increases. But in all cases $z'_n - y_n > \Delta_n$, i.e. $\phi > 1$.

In order to determine quantitatively the effect of a plate, we must know the actual composition γ of the vapour as a function of x. In general γ will vary from point to point of the plate, except at the plate immediately above or below the inlet, at which the vapour will be homogeneous. Hausen has shown that the farther away we are from the inlet the nearer γ approaches a definite limiting curve. Moreover, γ will also depend on whether the liquid flows in the same direction on each plate or whether it changes its direction from plate to plate. The greatest values of $z'_n - y_n$ are obtained when the direction of flow is uniform.

Fig. 127 shows the equilibration ratio ϕ for various cases as a function of $\beta = (m_G/m_L)b$. The upper curves were computed for an efficiency $\epsilon = 1$, the lower curves for $\epsilon = 0{\cdot}5$. It will be noted that, for $\beta = 1$, i.e. when the equilibrium curve is parallel to the working line, case (*a*)

gives $\phi = 2$ and case (b) $\phi = 1{\cdot}5$, when $\epsilon = 1$. In this case, a plate of the new type has an effect twice as great or one and a half times as great as an old plate, according as the direction of flow of the liquid is the same on each plate or varies from one plate to the next.

In a plant for separating air, it is clear that the effect of plates near the bottom of the column will be much greater than near the top, as

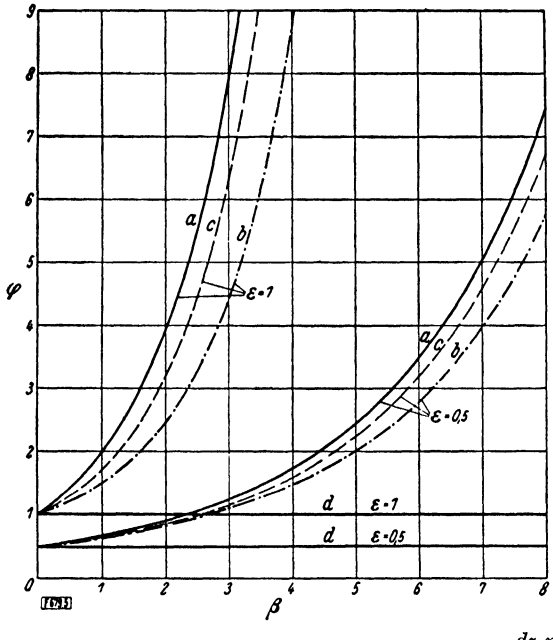


FIG. 127. Equilibration ratio ϕ as a function of $\beta = \dfrac{dz}{dx}\dfrac{m_G}{m_L}$ for efficiencies $\epsilon = 1$ and $0{\cdot}5$

a Direction of liquid flow the same on all plates; no stirring
b Direction of liquid flow alternating from plate to plate; no stirring
c Vapour stirred and homogeneous
d Vapour and liquid homogeneous

the equilibrium curve is much steeper in the region of high oxygen concentrations. This is illustrated in Fig. 128, which shows ϕ as a function of the position of the plate in the top half of a double column for separating air. The abscissae are nitrogen concentrations, so that the right-hand side of the figure corresponds to the top of the upper column.

On the basis of rather intricate calculations, Hausen† gives the following approximate graphical method for determining the change of composition undergone by a vapour in passing through a plate, on

† H. Hausen, *Actes du VII*ième *Congrès International du Froid*, La Haye, 1936, vol. i, p. 349.

which the liquid has a definite direction of flow and on which stirring is eliminated. Hausen supposes that the efficiency ϵ of the plates is known. He then introduces two magnitudes Φ and A as follows:

For plates on all of which the direction of flow is the same

$$\Phi = \frac{2\epsilon}{2-\epsilon}, \qquad A = \tfrac{1}{6}\Phi. \tag{15}$$

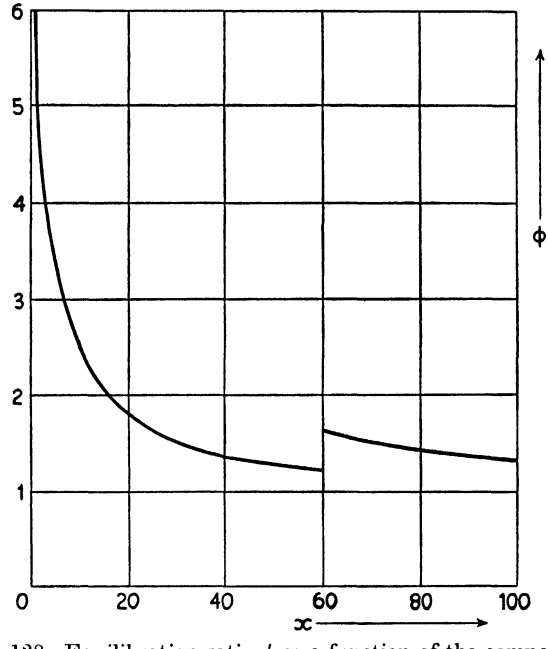


FIG. 128. Equilibration ratio ϕ as a function of the composition of the liquid x in the upper part of a double air column

For plates on which the direction of flow alternates

$$\Phi = \frac{2}{3}\frac{\epsilon(2-\epsilon)}{1+(1-\epsilon)(2-\epsilon)}, \qquad A = \Phi\frac{4}{15}\frac{5(1-\epsilon)+\epsilon^2}{(2-\epsilon)^2}. \tag{16}$$

The change in composition of a vapour passing through a plate can then be determined in a number k of stages. The greater k, the greater the accuracy, but usually $k = 2$ or 3 will be sufficient.

On a separate graph (Fig. 129) draw a vertical line of unit length on an arbitrary scale, beginning from a zero point O. From O draw a straight line parallel to the working line and cut off lengths OQ and OP to right and left of O, the vertical projections of which are equal to

$$\frac{\Phi}{2k}(1+kA) \quad \text{and} \quad \frac{\Phi}{2k}(1-kA) \quad \text{respectively.}$$

Then join PR and QR. If we now introduce between the working line and the equilibrium curve a series of straight lines alternately parallel to PR and QR (see Fig. 129), k such pairs of straight lines will give us the change in composition of a vapour passing through the plate.

For the case of $\epsilon = 1$, Φ for uniform motion is 2 and for alternate motion 2/3, and the corresponding values of A are 1/3 and 8/45 respectively. The method will then give the 'effect' of the plate.

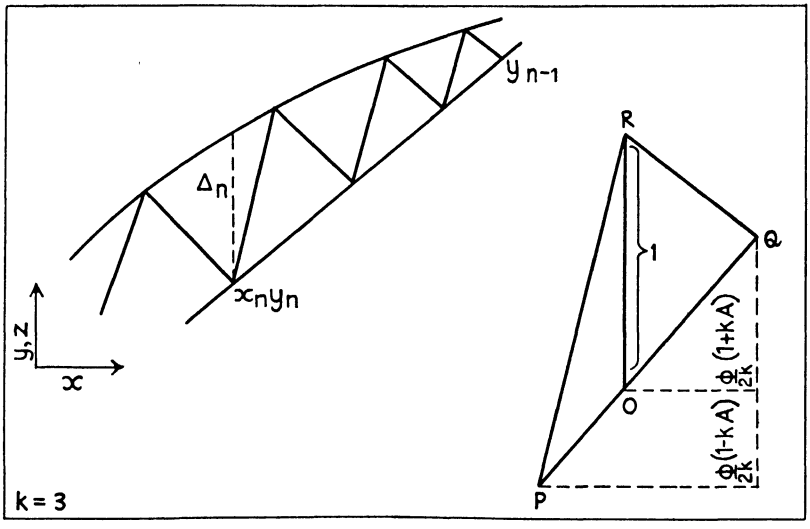


FIG. 129. Graphical method of determining the effect of a plate with inhomogeneous liquid

The construction is exact for $\beta = 1$ and is fairly accurate when β is not far removed from unity. But it assumes that the influence of the homogeneous vapour at the inlet is negligible. For the plate immediately above the inlet we can use the same construction with

$$\Phi = e^{-\epsilon} - 1, \qquad A = 1 - 2\frac{1-(1-\epsilon)e^{-\epsilon}}{(e^{-\epsilon}-1)^2}. \tag{17}$$

A method devised for the same purpose by Kirschbaum and Quade† obviates some of the mathematical difficulties by a more graphical treatment and at the same time eliminates the approximations. However, for practical purposes it is slower than Hausen's simple construction.

W. K. Lewis, Jr.,‡ in a paper published in the same year as that of Hausen, arrives at the same values for the equilibration ratio ϕ as a function of $\beta = dz/dx.m_G/m_L$ and of the efficiency of the plate ϵ.

† Loc. cit.

‡ W. K. Lewis, Jr., *Ind. Eng. Chem.* **28**, 399 (1936).

According to Lewis, and in most of the American literature, the expression ϕ is called the overall or plate efficiency, whereas the ratio of the actual change to the maximum possible change in vapour composition, which we have called the efficiency ϵ, is termed the point or Murphree efficiency.† The use of the term efficiency for ϕ is unfortunate, as this expression does not describe an efficiency at all, as may

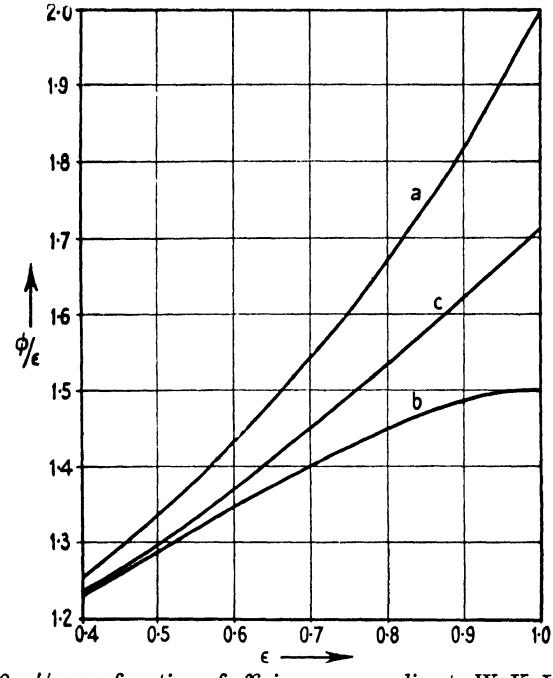


FIG. 130. ϕ/ϵ as a function of efficiency ϵ according to W. K. Lewis, Jr. for $\beta = 1$, i.e. when the working line is parallel to the equilibrium curve

a Direction of liquid same on all plates; no stirring
b Direction of liquid alternating from plate to plate; no stirring
c Vapour stirred and homogeneous

be seen from the fact that it can be considerably greater than unity. ϕ is the ratio of the actual change in vapour composition to the maximum change that could take place on a particular kind of plate on which the liquid is homogeneous. If E is the effect of the actual plate, and E_1 that of a plate with homogeneous liquid, then

$$\phi = \frac{\epsilon E}{E_1}. \tag{18}$$

Thus $\phi/\epsilon = E/E_1$ is the ratio of the effect of the plate under consideration to one with homogeneous liquid having the same efficiency. Fig. 130

† E. V. Murphree, ibid. **17**, 747 (1925).

shows ϕ/ϵ according to Lewis for the three cases when $\beta = 1$, i.e. when the working line and the equilibrium line are parallel.

Lewis's calculation is based on bubble-cap plates, whereas Hausen considers perforated plates. However, the means by which vapour and liquid are contacted do not feature in either of the papers and the results should be the same in both cases.

Plates on which the liquid is maintained inhomogeneous and made to flow in a definite direction may be designed in various ways. In one of the most popular forms the liquid is made to flow along an annular surface, which has a vertical partition near the point at which the liquid is introduced. The partition causes the liquid to flow in one direction only, until it comes to the outlet, from which it is delivered on to the next plate. Evidently, by a suitable distribution of the partitions, the liquid may be constrained to flow in the same sense around each plate, or it may be made to change its direction from one plate to another.

3. Equilibration of liquid and vapour

We have seen that the change in composition, undergone by a vapour in traversing a plate, can be expressed as the product of the effect E of the plate and a factor ϵ called the efficiency. In the last two sections it was shown how the effect of a plate may be determined and how it may be increased by appropriate designing. But up till now the efficiency has figured as a known and constant quantity, which was carried in the equations without comment, and on the numerical value of which no light was shed. Since the property of a plate which interests us most, the actual change in composition that it brings about, is equal to the product of effect and efficiency, an increase in the one may quite well be counteracted by a decrease in the other.

The vagueness with which efficiency is generally treated is due to the considerable mathematical difficulties inherent in determining it. These difficulties, which were openly faced and, in part at least, overcome by Bošnjaković,† consist in the fact that every equilibration process between a binary liquid and its vapour comprises the simultaneous transfer of heat and matter from one phase to another. It follows from this that neither diffusion equations, based on differences of composition alone, nor equations of heat transfer, based only on differences of temperature, can give a complete account of the phenomena.

† F. Bošnjaković, *Technische Mechanik und Thermodynamik*, **1**, 358 (1930); *Forschung auf dem Gebiet des Ingenieurwesens*, **3**, 145 and 213 (1932). M. Ruhemann, *Physica*, **4**, 1157 (1937).

On the plates of a column the liquid is continually traversed by bubbles of vapour, which, at the moment when they enter the liquid, are not in equilibrium with it. We wish to elucidate what factors are at work in promoting equilibration, and what is the specific influence of each factor. Such factors may be the size of individual bubbles, their velocity, or, which comes to the same thing, the time that they spend in contact with the liquid, their composition on entering the plate and the composition they would have if they were in equilibrium with the liquid, their temperature and the temperature of the liquid, etc.

If a binary liquid be in contact with a vapour consisting of the same components, molecules of both kinds will be continually escaping from, and condensing upon, the liquid surface. These two phenomena may be termed *evasion* and *invasion* respectively. The amounts of the components 1 and 2 passing out of the liquid through unit surface in the time dt may be written

$$dm_1^\beta = \beta_1 x_1\, dt, \qquad dm_2^\beta = \beta_2 x_2\, dt, \tag{19}$$

where x_1 and x_2 are the concentrations of the two components and β_1 and β_2 are known as *evasion coefficients* and may depend on temperature and composition of the liquid and on its state of motion.

In the same way, the amount of each component entering the liquid may be written

$$dm_1^\gamma = \gamma_1 y_1 p\, dt \quad \text{and} \quad dm_2^\gamma = \gamma_2 y_2 p\, dt, \tag{20}$$

where y_1 and y_2 are the concentrations of 1 and 2 in the vapour at pressure p, and γ_1 and γ_2 are known as *invasion coefficients*. Since the γ's refer to the vapour phase, in which interaction between molecules is relatively small, it is assumed that γ_1 and γ_2 are independent of the composition of vapour and liquid. The invasion dm^γ is then proportional to the partial pressure of the component in the vapour phase, which is equal to yp.

If liquid and vapour are in equilibrium, no net transfer will take place, so that

$$dm = dm_1^\beta + dm_2^\beta - dm_1^\gamma - dm_2^\gamma = 0, \tag{21}$$

or, with equations (19) and (20),

$$\beta_1 x_1 + \beta_2 x_2 - \gamma_1 y_1 p - \gamma_2 y_2 p = 0. \tag{22}$$

A similar 'balance equation' must hold for each of the components separately, as the same number of molecules of each kind will enter and leave the liquid. Therefore

$$\beta_1 x_1 - \gamma_1 y_1 p = 0, \tag{23}$$

$$\beta_2 x_2 - \gamma_2 y_2 p = 0. \tag{24}$$

The last equations can be written in the form

$$\beta_1 = \gamma_1 p y_1 / x_1, \tag{25}$$

$$\beta_2 = \gamma_2 p y_2 / x_2. \tag{26}$$

We have thus expressed the β's in terms of the γ's, the composition of the phases and the total pressure of the vapour. But we must note that the terms entering in these equations have *equilibrium values*; that is to say, the β's and γ's, in this particular case, refer to the same temperature, p is the vapour pressure of the liquid at this temperature, and y_1, y_2 are the concentrations of both components of a vapour in equilibrium with a liquid of composition x_1, x_2. To remind us of this, we shall add a bar to p, y, and γ in these equations:

$$\beta_1 = \bar{\gamma}_1 \bar{p} \frac{\bar{y}_1}{x_1}, \tag{27}$$

$$\beta_2 = \bar{\gamma}_2 \bar{p} \frac{\bar{y}_2}{x_2}. \tag{28}$$

The bar indicates that those values of p, y, and γ must be taken which hold for equilibrium with the liquid phase chosen.

Now suppose that the equilibrium of the system is disturbed. This means that the temperature of the vapour differs from that of the liquid and (or) the composition of the vapour differs from that of a vapour in equilibrium with the liquid. The result may be that liquid evaporates, or that vapour condenses, or that merely the compositions of the phases change. In general, the relative amounts and compositions of the phases will both be altered, as usually happens in a rectifying column.

In the general case, the amount of the substance 1 transferred from the liquid to the vapour in the time dt through unit surface will be

$$dm_1 = dm_1^\beta - dm_1^\gamma = (\beta_1 x_1 - \gamma_1 p y_1)\, dt, \tag{29}$$

and for the substance 2,

$$dm_2 = dm_2^\beta - dm_2^\gamma = (\beta_2 x_2 - \gamma_2 p y_2)\, dt. \tag{30}$$

p is here the actual pressure and need not be the same as the equilibrium vapour pressure $\bar{p}$ of the liquid with a composition x_1, x_2.

We can now replace β_1 and β_2 by their equilibrium values, as given in equations (27) and (28), so that

$$\frac{dm_1}{dt} = \bar{\gamma}_1 \bar{p} \bar{y}_1 - \gamma_1 p y_1, \tag{31}$$

$$\frac{dm_2}{dt} = \bar{\gamma}_2 \bar{p} \bar{y}_2 - \gamma_2 p y_2, \tag{32}$$

or, if we introduce partial pressures with $p_1 = py_1$, $p_2 = py_2$,

$$\frac{dm_1}{dt} = \bar{\gamma}_1 \bar{p}_1 - \gamma_1 p_1, \tag{33}$$

$$\frac{dm_2}{dt} = \bar{\gamma}_2 \bar{p}_2 - \gamma_2 p_2, \tag{34}$$

and the total amount of both components together, passing from the liquid to the vapour phase in time dt, will be

$$dm = dm_1 + dm_2, \tag{35}$$

and $dm \gtreqless 0$.

With the help of the kinetic theory of gases, the following relationship may be deduced for γ as a function of the absolute temperature T and the molecular weight μ:

$$\gamma = g \frac{1}{\sqrt{(\mu T)}}; \tag{36}$$

g depends only on the state of motion of liquid and vapour, and is therefore the same for both components. Similarly, both components of a single phase are at the same temperature. Equations (33) and (34) may therefore be written in the form

$$\frac{dm_1}{dt} = \frac{g}{\mu_1^{\frac{1}{2}}} \left(\frac{\bar{p}_1}{T_L^{\frac{1}{2}}} - \frac{p_1}{T_G^{\frac{1}{2}}} \right), \tag{37}$$

$$\frac{dm_2}{dt} = \frac{g}{\mu_2^{\frac{1}{2}}} \left(\frac{\bar{p}_2}{T_L^{\frac{1}{2}}} - \frac{p_2}{T_G^{\frac{1}{2}}} \right), \tag{38}$$

where T_L and T_G are the temperatures of the liquid and vapour respectively, and

$$\frac{dm}{dt} = \frac{dm_1}{dt} + \frac{dm_2}{dt}.$$

For water boiling in an open vessel, g was observed to be about 0·8 [(°abs.)$^{\frac{1}{2}}$/hr.]. It is probable that g is fairly close to this value for any type of perforated rectifying plate.

We may use equations (37) and (38) to compute the efficiency of a plate in a column. For if we can solve the equations for a particular case, we know m_1 and m_2 as a function of t. If we then determine the time during which the vapour is in contact with the liquid on the plate, we can find out how much of each component passes from one phase to the other, and thus calculate the actual change of composition of the phases.

Apart from the molecular weights of the components, dm/dt depends on the temperatures of both phases separately, on the actual partial

pressures in the vapour and the partial pressures that would subsist in equilibrium with the liquid on the plate. Since the partial pressure is defined as the product of total pressure and concentration, it contains two variables in itself. Thus, equations (37) and (38) contain a large number of variables, the mutual dependence of which is difficult to determine. To obtain a figure for the efficiency of a plate, without going through very intricate calculations, we shall have to approximate rather crudely.

If we take the case of oxygen–nitrogen mixtures, the molecular weights of the components are 32 and 28 respectively. As only the square root of μ enters into the equations, we shall not go far wrong if we put $\mu_1 = \mu_2 = 30$.

In the upper column of a rectifying plant, in which the pressure is 1 atm., the temperature in the condenser is 90° abs. and the nitrogen leaves the top of the column at about 77·5°. The temperature head between the top and bottom of the column is therefore 12·5°, or 16·2 per cent., and it is the square root of the temperature head which is of interest for our equation. This corresponds to a change in composition of 100 per cent. between the top and bottom of the column. A similar relation between the changes of temperature and composition will hold for a single plate. So we can, without incurring a very considerable error, put $T_L = T_G = \text{const.}$ for a single plate.

As regards the pressures that enter into each equation, we have no choice but to pretend that they are equal, though we know quite well that they are not. But any other assumption would complicate matters too much. It can be shown that the error incurred will not distort the results very far.

If we make all these simplifying assumptions, equation (37) boils down to the following simple form:

$$\frac{dm_1}{dt} = \frac{gp}{\sqrt{(\mu T)}}(z_1 - y_1), \tag{39}$$

in which we suppose 1 to refer to nitrogen. We assume $g = 0{\cdot}8$, $p = 1$ atm., and $\mu = 30$. z_1 is the nitrogen concentration in a vapour in equilibrium with the liquid on the plate, and y_1 the actual nitrogen concentration in the vapour at the time t.

To simplify matters still further, we shall assume that the heats of evaporation of oxygen and nitrogen are the same, as we did earlier in this chapter. The effect of this is that the size of each bubble remains unchanged during its passage through the liquid. Only its composition

changes, and we have what we may term a case of 'pure rectification'. Thus

$$\frac{dm_1}{dt}+\frac{dm_2}{dt}=0. \tag{40}$$

Since the composition of the liquid is regarded as a constant with regard to time, the only variable in equation (39) is y_1, and we may write

$$\frac{dm_1}{dt}=a(z_1-y_1) \tag{41}$$

with

$$a=\frac{gp}{\sqrt{(\mu T)}}. \tag{42}$$

Now let y_0 be the nitrogen concentration in the bubble when it enters the plate at $t=0$. Let M be the constant mass of the bubble and S its surface. Then at a given time $t>0$,

$$M_1=My_0+Sm_1, \tag{43}$$

$$y_1=M_1/M=y_0+Sm_1/M, \tag{44}$$

or, if we put $M/S=m$, $$y_1=y_0+m_1/m. \tag{45}$$

Equation (41) then becomes

$$dm_1/dt=a(z_1-y_0-m_1/m). \tag{46}$$

At $t=0$, $m_1=0$ and $y_1=y_0$; and at $t=\infty$, $y_1=z_1$. Therefore the solution of (46) is

$$m_1=(z_1-y_0)m(1-e^{-at/m}). \tag{47}$$

Now $(z_1-y_0)m$ is the total amount of nitrogen that must enter the bubble per unit surface in order that complete equilibrium may be attained. Therefore

$$q=\frac{m_1}{m(z_1-y_0)} \tag{48}$$

is the degree of equilibrium reached up to the time t, and we may write

$$q=1-e^{-at/m}. \tag{49}$$

Since $m_1/m=y_1-y_0$ from equation (45),

$$q=\frac{y_1-y_0}{z_1-y_0}. \tag{50}$$

Thus, at the moment of leaving the liquid, q is identical with the efficiency ϵ.

If we replace the mass m per unit surface by the radius r of the bubble, which we assume to be spherical, and reduce both quantities to the same units, we finally obtain

$$\frac{a}{m}=68{\cdot}4\sqrt{\left(\frac{T}{\mu}\right)}\frac{g}{r}, \tag{51}$$

where r is in centimetres.

We see from equation (49) that the time required to produce a certain degree of equilibration q is independent of the original composition of liquid and vapour. This means that, at any rate in our approximation, the efficiency of all the plates of a column is the same.

To ascertain how far these formulae are correct, and more especially how far the approximations were justified, we can use the results here obtained to compute the efficiency of the plates of a certain column, and then see how far the figures tally with the known efficiency of the column as a whole. We shall take the large Linde air column described in Chapter VII, since the dimensions of this plant are well known. As we saw, the plant separates 6,500 cu. m. of air per hour. The pressure in the lower column is 5 atm., that in the upper column 1 atm. The perforation of the plates is 0·8 mm. in diameter.

By taking the mean temperature in each column and assuming $g = 0{\cdot}8$, we obtain the following values of a/m:

$$\text{lower column: } a/m = 81;$$

$$\text{upper column: } a/m = 77.$$

This gives us the following table for q as a function of t in seconds. l refers to the lower and u to the upper column.

TABLE 21. *Degree of Equilibration q on the Plates of a Large Linde Air Column as a Function of Time*

t (*sec.*)	q_l	q_u
0·01	0·555	0·537
0·02	0·802	0·785
0·03	0·910	0·901
0·04	0·962	0·954
0·05	0·983	0·979
0·06	0·992	0·991

The period of time required for equilibrium to be attained within a few per cent. is thus seen to be of the order of some hundredths of a second.

We must now ascertain how long the vapour is really in contact with the liquid on the plate. From the known quantities of vapour moving in the various parts of the column, we find that, in the space between the plates, the velocity of the vapour is

$$v_l = 5{\cdot}325 \times 10^4 \text{ cm.}^3/\text{sec.},$$

$$v_u = 26{\cdot}9 \times 10^4 \text{ cm.}^3/\text{sec.},$$

in the lower and upper columns respectively.

To determine the velocity of the bubbles on the plates, we must

know the effective cross-sections of the vapour in the liquid. This cannot be determined accurately. For the bubbles will remain bubbles in the liquid and will only fill a portion of the cross-section of the plate itself. Since only part of the plate is perforated and we have no quantitative data as to how the bubbles spread out in the liquid, we can only make a rough guess at the effective cross-section. We shall assume, rather arbitrarily, that the effective cross-section is one-third of the total cross-section of the column. We then find for the period of time during which the vapour is in contact with the liquid,

$$t_l = 0{\cdot}042 \text{ sec.},$$

$$t_u = 0{\cdot}010_7 \text{ sec.}$$

This gives us, with the help of Table 21,

$$\epsilon_l = 0{\cdot}966,$$

$$\epsilon_u = 0{\cdot}556.$$

We see that the efficiency in the lower column is practically unity, whereas it is much smaller in the upper column.

The theoretical number of plates for $\epsilon = 1$ has been computed for this particular column by A. Weissberg.† On the other hand, we know the actual number of plates in the upper and lower columns.‡ The ratio of these figures should give us the actual efficiency of the plates. The data are collected in Table 22 and compared with the values we have just computed.

TABLE 22. *Efficiency of the Plates of a Large Linde Air Column*

	n_t	n_a	ϵ_a	ϵ
Lower column . .	23	24	0·96	0·966
Upper column . .	14	36	0·39	0·556

n_t signifies the theoretical number of plates for $\epsilon = 1$, according to Weissberg's calculations; n_a is the actual number. $\epsilon_a = n_t/n_a$ may be called the actual efficiency of the plates, ϵ is the efficiency we have calculated.

We see that ϵ_a and ϵ are of the same order of magnitude, which seems to corroborate the line taken in the calculations. The agreement in the lower column is far closer than the accuracy of the calculations justifies and must therefore be taken as somewhat fortuitous. The

† A. Weissberg, *Journal of Technical Physics* (Russian), **4**, 1204 (1934).

‡ S. Gersch, *Glubokoe Okhlazhdenie* (Low-temperature Engineering), part ii, Moscow, 1937.

agreement for the upper column is probably all that we have a right to expect, but it is actually rather better than it seems. For apart from the fact that the manufacturers would tend to add a few plates in the final column, to make sure of obtaining the required purity of the products, there is another much more important reason why the efficiency must needs be smaller in this column than the calculated figure. This is connected with the fact, hitherto neglected, that air is not really a binary mixture at all. We shall see in the next chapter that the rare gases, in particular argon, play a very important role in the functioning of an air plant and greatly reduce the efficiency of the upper column.

The above calculation was based on the assumption that perforated plates were used in the column. For the case of bubble-cap plates Geddes† has developed a method for determining the point efficiency ϵ as a function of the dimensions of the slots in the bubble-caps, their submergence under the surface of the liquid and the physical characteristics of the liquid and vapour. His result, which can be written in the form

$$\epsilon = 1-e^{-3Kt/r}, \tag{52}$$

is seen to be similar to equation (49), but the exponent contains, apart from the time t which the bubble spends in the liquid, and the radius r of the bubble, the overall mass transfer coefficient K between vapour and liquid through the surface of the bubble. K itself is composed of a gas film coefficient k_g and a liquid film coefficient k_l through the relation

$$1/K = 1/k_g+c_i/c_i' k_l, \tag{53}$$

where c_i and c_i' are the concentrations at the interface of the gas film and liquid film respectively.

Geddes shows how these film coefficients can be calculated, as well as the time of contact and the radius of the bubbles. His calculated efficiencies agree well with experimental results obtained with a number of rectification and absorption columns.

Equation (52) would reduce to (49) if the complex mass transfer coefficient K had the simple form

$$K = \frac{gp}{\gamma\sqrt{(\mu T)}}, \tag{54}$$

where γ is the density of the vapour and the other terms have the same meaning as in equation (49). Assuming as previously that

$$g = 0{\cdot}8\ (°\text{K.})^{\frac{1}{2}}/\text{hr.},$$

† R. L. Geddes, *Amer. Inst. Chem. Eng.*, p. 79 (1946).

and transforming to the units used in Geddes's paper, we obtain

$$K = \frac{6{\cdot}1 \times 10^{-3} p}{\gamma\sqrt{(\mu T)}} \text{ ft./sec.} \tag{55}$$

This simple formula can be applied to an alcohol–water column which is the only example of a simple fractionation process with a binary mixture treated in Geddes's paper. Inserting the appropriate values in equation (55), we find $K = 0{\cdot}067$. With the full calculation and working the column under various conditions, Geddes finds values of K between 0·066 and 0·093.

IX

AIR AS A TERNARY MIXTURE

1. The influence of argon on the production of oxygen and nitrogen

THE composition of atmospheric air, as given in Table 1, justifies us in considering it, to a first approximation, as a binary mixture of oxygen and nitrogen. As long as our aims are limited to the production of oxygen and nitrogen of a purity compatible with technical requirements, the presence of krypton and xenon in atmospheric air never becomes manifest at all, while the influence of neon and helium, though appreciable, is easily eliminated. Argon, however, which is present in a concentration of just under 1 per cent., affects the production of oxygen and nitrogen to a greater extent than might be expected. This fact, which was ascertained by Hausen† as late as 1934, will concern us in the present section.

There are two distinct attitudes which may be adopted towards the rare gases as constituents of atmospheric air. One is to consider their influence on the production of pure oxygen and nitrogen, the other to find ways and means of extracting them in a pure condition. In the first case the rare gases are considered as undesirable impurities, in the second they are themselves primary products of separation. This second question will be treated in the next section.

In spite of the large number of components present in the atmosphere, their concentrations and thermal properties are such that we are never forced to bear them all in mind simultaneously. When discussing argon we are at liberty to forget the presence of other rare gases; in considering neon and helium we can neglect oxygen and argon. Only in very exceptional cases need we turn our attention to more than three components at the same time. Though these components will differ according to the particular problem treated, yet for all practical purposes we can confine ourselves to ternary mixtures.

The presence of 0·93 per cent. of argon in the atmosphere makes it impossible to obtain pure oxygen and pure nitrogen simultaneously in the plants described in Chapter VII. The one or the other product must needs be contaminated with argon. If all the argon is collected with the oxygen, the latter cannot be more than 95 per cent. pure; if it is extracted with the nitrogen and the oxygen is pure, the purity of the

† H. Hausen, *Forschung auf dem Gebiet des Ingenieurwesens*, **5**, 290 (1934).

nitrogen cannot exceed 98·7 per cent. Since the boiling-point of argon lies between the boiling-points of oxygen and nitrogen, we can in principle choose with which product it will emerge from the plant. In the general case both products will be more or less contaminated.

This is the first and most obvious reason why the presence of argon cannot be neglected in the separation of oxygen and nitrogen. The second may be deduced from the following. Since the boiling-point of argon lies between those of oxygen and nitrogen, the boiling- and dew-curves of argon–oxygen mixtures and of argon–nitrogen mixtures lie closer together than those of oxygen–nitrogen mixtures. We know that, the closer together the boiling-curve and dew-curve of a mixture, the more difficult that mixture is to separate, that is to say, the smaller will be the effect of each plate and therefore the more plates will be needed. We may thus conclude that on those plates of an air column on which pure oxygen and pure nitrogen are to be obtained, it is not so much oxygen and nitrogen that are being separated, but oxygen and argon or nitrogen and argon, and, in view of the proximity of the boiling- and dew-curves of these mixtures, this separation will require a considerable number of plates.

Indeed, if we compare the (T, x) diagrams of oxygen–nitrogen and oxygen–argon in Figs. 30 and 32, we see immediately that the equilibrium curves of the latter are very much closer than those of the former. For example, an oxygen–nitrogen liquid mixture at 1 atm. containing 80 per cent. of oxygen is in equilibrium with a vapour containing 49 per cent. oxygen, whereas a liquid mixture with 80 per cent. oxygen and 20 per cent. argon is in equilibrium with a vapour containing 71 per cent. oxygen and 29 per cent. argon. Similar differences, though less pronounced, hold good in argon–nitrogen mixtures, when compared with those of oxygen and nitrogen.

A more detailed analysis will show that, under certain circumstances, a very considerable accumulation of argon will occur in certain parts of an air column, and that the removal of this argon from the oxygen or nitrogen product is a serious matter. It will then become clear that the apparently low efficiency of the plates in the upper Linde column, noted at the end of Chapter VIII, is, in fact, due to a low effect, resulting from the preponderance of argon on certain plates.

The full equilibrium diagram of the ternary system oxygen–nitrogen–argon has not yet been determined experimentally. Referring back to Chapter II, we see that the three binary systems have been studied fairly accurately. For O_2–N_2 we have the classical work of Dodge and

Dunbar, for A–N_2 the work of Holst and Hamburger, and for A–O_2 preliminary measurements of Inglis and a more recent and detailed paper by Bourbo and Ischkin. Before the latter work appeared, Hausen† constructed an equilibrium diagram of the ternary system on the basis of existing experimental results, coupled with theoretical considerations involving an integration of the Duhem–Margules equation. He represented the results of his calculations in the form of a triangular diagram with two superimposed systems of coordinates, as described in Chapter II and shown in Fig. 16.

Hausen developed his theory of the separation of ternary mixtures not so much with a view to calculating the number of plates required as in order to obtain an insight into the increase and decrease of the concentrations of the several components as the mixture moves along the column. His theory does not therefore aim at determining the compositions in steps from one plate to the next, but develops continuous smooth curves giving the composition of the mixture. This is equivalent to assuming a very low efficiency of the plates or, which comes to the same thing, a packed column with no plates at all. The smooth curves so obtained can be broken up later into discontinuous steps if required.

Consider a portion of a rectifying column containing oxygen, nitrogen, and argon. In a certain section let x_o and x_a be the oxygen and argon concentrations in the liquid, and y_o and y_a the concentrations in the vapour. z_o and z_a are the equilibrium vapour concentrations corresponding to a liquid of the composition x_o and x_a. The nitrogen concentrations x_n, y_n, and z_n are determined by the fact that the three x's, y's, and z's must add up to unity. Let M_l be the amount of liquid and M_g the amount of vapour flowing past a given section in a given time. As in the case of oxygen–nitrogen mixtures, we may assume as a first approximation that the heats of evaporation of the three components are the same. It can then be proved as before that M_l and M_g are constant throughout the column. In considering the balance equations of a portion of the column, we can then neglect the balance of heat and only take the balance of mass and composition into account. Then, if $\bar{x}_o$, $\bar{x}_a$; $\bar{y}_o$, $\bar{y}_a$ are the given concentrations of liquid and vapour on a certain section, the concentrations x_o, x_a; y_o, y_a on any other section will be given by the equations

$$\left.\begin{aligned} M_l x_o - M_g y_o &= M_l \bar{x}_o - M_g \bar{y}_o, \\ M_l x_a - M_g y_a &= M_l \bar{x}_a - M_g \bar{y}_a, \end{aligned}\right\} \qquad (1)$$

† H. Hausen, *Forschung auf dem Gebiet des Ingenieurwesens*, **6**, 9 (1935).

which may be written

$$\left.\begin{aligned} y_o &= \bar{y}_o - \frac{M_l}{M_g}\bar{x}_o + \frac{M_l}{M_g}x_o, \\ y_a &= \bar{y}_a - \frac{M_l}{M_g}\bar{x}_a + \frac{M_l}{M_g}x_a. \end{aligned}\right\} \tag{2}$$

Now suppose the column to contain plates of the 'old-fashioned' type, on each of which the liquid is homogeneous. It can be proved

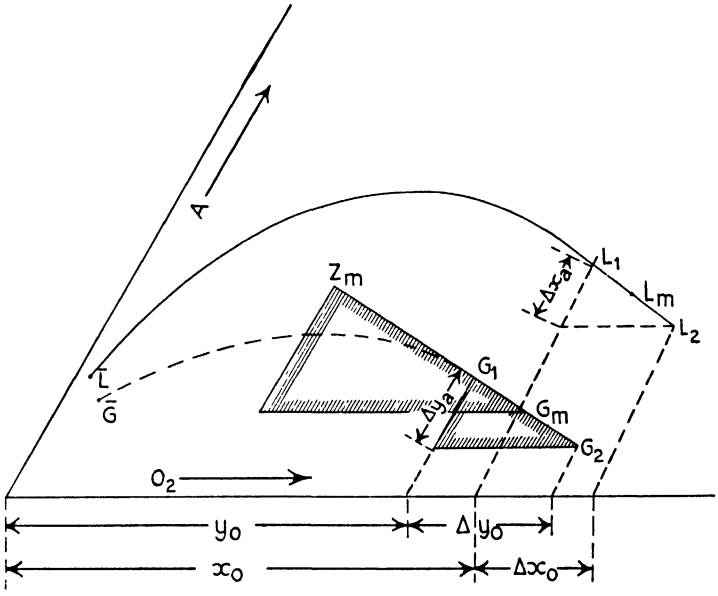


FIG. 131. Graphical method for determining rectification curves of ternary mixtures

that the efficiency ϵ of a plate is the same for each component. Then the change of composition undergone by a vapour on passing through a plate will be

$$\left.\begin{aligned} \Delta y_o &= \epsilon(z_o - y_o), \\ \Delta y_a &= \epsilon(z_a - y_a), \end{aligned}\right\} \tag{3}$$

so that

$$\frac{\Delta y_o}{\Delta y_a} = \frac{z_o - y_o}{z_a - y_a} \tag{4}$$

irrespective of ϵ. This equation will also hold when $\epsilon \ll 1$.

Now consider the diagram in Fig. 131, in which oxygen concentrations are measured along the base and argon concentrations along the left side. Let $\bar{L}$ and $\bar{G}$ be two points with the concentrations $\bar{x}_o$, $\bar{x}_a$ and $\bar{y}_o$, $\bar{y}_a$ at a certain section of the column. Then, as we proceed along the column, the points L and G, representing the composition of liquid and gas on various sections, will describe curves. If the

changes in composition on each plate are sufficiently small, these cur will be approximately smooth.

Suppose Δy_o and Δy_a to signify changes in composition of the extending over a number of very small steps. Then the y's and z's (4) must be replaced by mean values, so that

$$\frac{\Delta y_o}{\Delta y_a} = \frac{z_{om} - y_{om}}{z_{am} - y_{am}}.$$

Suppose the curves have already been determined from the points and $\bar{G}$ to L_1 and G_1 with the coordinates x_o, x_a and y_o, y_a respective and we wish to determine their further course. We can first cho arbitrarily an increment Δx_o. Then, according to (2), Δy_o will be giv as $\Delta y_o = \Delta x_o M_l/M_g$. We now extrapolate the liquid curve to where believe the middle of this step to be, reaching a point L_m with coordinates x_{om}, x_{am}. The vapour in contact with this liquid will represented by a point G_m with the coordinates y_{om}, y_{am}. Let the po Z_m with the coordinates z_{om}, z_{am} represent a vapour in equilibrium w L_m. If we now join $Z_m G_1$, the projection of this straight line will p through G_m and thus also through the required point G_2 with coordinates $y_o + \Delta y_o$ and $y_a + \Delta y_a$. This is proved from the fact th in the shaded triangles, which are similar, equation (5) is fulfill Since, according to (2),

$$\Delta y_a/\Delta y_o = \Delta x_a/\Delta x_o,$$

the increment $L_1 L_2$ of the liquid curve must be laid parallel to that the vapour curve and should pass through the extrapolated point which it usually does. If it does not, the construction must be repea and L_m more judiciously chosen.

The lines for the liquid and vapour obtained in this way are kno as *rectification curves*. As may be seen from equations (2), they depe on the concentrations x_o, x_a; y_o, y_a and the ratio M_l/M_g.

Let us now apply this method to the practical case of atmosphe air. We shall first consider a single column of the type described Chapter VI, p. 141, and lay down as a condition that we wish to obt pure oxygen in the evaporator.

If $\bar{x}_o$, $\bar{x}_a$ and $\bar{y}_o$, $\bar{y}_a$ are the compositions of liquid and vapour at top of the single column, and $\underline{x}_o$, $\underline{x}_a$; $\underline{y}_o$, $\underline{y}_a$ the composition in evaporator, we have

$$\bar{x}_o = 20{\cdot}9, \qquad \underline{x}_o = \underline{y}_o = 100,$$
$$\bar{x}_a = 0{\cdot}93, \qquad \underline{x}_a = \underline{y}_a = 0.$$

$\bar{y}_o$ can be chosen arbitrarily within certain limits, but it can in no c

be smaller than 6·15 per cent., which would be the oxygen concentration of a vapour in equilibrium with liquid air.

Equations (2), referring to the top and bottom of the column, may now be written as follows:

$$\left.\begin{aligned} y_o &= \bar{y}_o - \frac{M_l}{M_g}(\bar{x}_o - x_o), \\ y_a &= \bar{y}_a - \frac{M_l}{M_g}(\bar{x}_a - x_a). \end{aligned}\right\} \qquad (7)$$

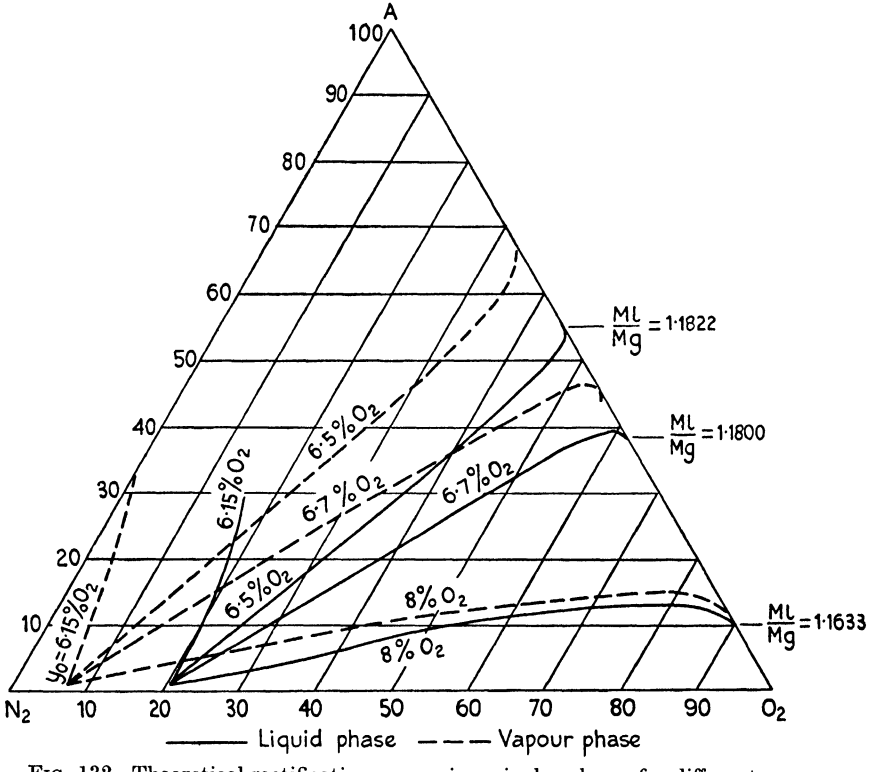


FIG. 132. Theoretical rectification curves in a single column for different oxygen contents of the nitrogen product

Since $\bar{x}_o$, x_o, and y_o are given, a choice of $\bar{y}_o > 6{\cdot}15$ per cent. determines M_l/M_g according to (7). Since $\bar{x}_a$, x_a, and y_a are given, $\bar{y}_a$ is also determined. For $\bar{y}_o = 6{\cdot}15$ per cent., $\bar{y}_a$ becomes 1·1 per cent.

In Fig. 132 the rectification curves are shown, as computed by Hausen with the construction given above, for various values of $\bar{y}_o$ ranging from 6·15 to 8 per cent., and the values of M_l/M_g deduced from the first part of (7). The full curves represent the liquid phase, the dotted lines are

for the vapour. These curves show the change in composition of the liquid and gaseous mixtures on their way down the column.

The first fact that strikes us is that the curves end along the argon–oxygen axis. Thus, as we expected, the final stages of the process consist in rectifying an argon–oxygen mixture, the nitrogen having been completely displaced by the argon.

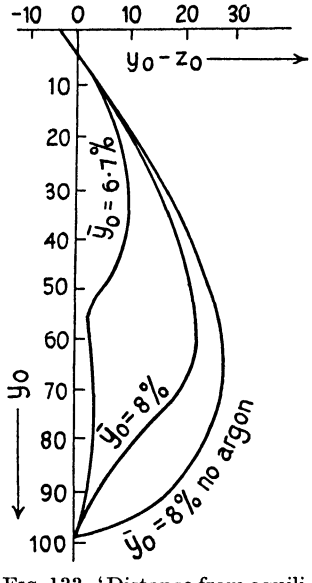


FIG. 133. 'Distance from equilibrium' in respect of oxygen in a single column as a function of the oxygen content of the vapour for different oxygen contents of the nitrogen product and for air free of argon

Secondly, even in the lowest curve, for $\bar{y}_o = 8$ per cent. O_2, a very considerable argon accumulation occurs in the column. From 0·93 per cent. at the top, the argon concentration rises to about 12 per cent. in the liquid and 15 per cent. in the vapour, before it finally decreases to zero at the bottom of the column.

If we choose $\bar{y}_o = 6{\cdot}7$ per cent., this effect is still more marked. The argon concentration rises to 39 per cent. in the liquid and 45 per cent. in the vapour. Finally, the curves bend down sharply and continue along the argon–oxygen axis.

If $\bar{y}_o$ is lowered to 6·5 per cent., the plant ceases to function. The curves bend round in the opposite direction and end at 84 per cent. argon in equilibrium with its vapour instead of pure oxygen. That is to say, we should obtain rich argon at the bottom of the column if we were in a position to maintain the ratio $M_l/M_g = 1{\cdot}1822$. We cannot do this, as we have not enough argon to remove at the bottom of the column. The curves for $\bar{y}_o = 6{\cdot}5$ per cent., and 6·15 per cent. have therefore no physical significance. Between the curves for $\bar{y}_o = 6{\cdot}5$ per cent. and 6·7 per cent. we could find one rectification curve to intersect the oxygen–argon axis without bending round at all. It has been shown that such lines exist for all values of $\bar{x}_o$, $\bar{x}_a$ and that they are almost straight. Hausen calls them *demarcation lines*, as they mark the limits up to which the column will work. Every point on the argon–oxygen axis marks the end of one and only one demarcation line.

We see further that the argon accumulation increases with increasing values of M_l/M_g, i.e. the more oxygen is removed from the base of the column.

In order to show the detrimental influence which the accumulation of argon in the column exerts on the effect of the plates, we can plot the 'distance from equilibrium' $y_o - z_o$, expressed in oxygen concentration, in any cross-section of the column, as a function of the oxygen concentration of the vapour. This has been done in Fig. 133 for oxygen concentrations of emerging vapour of 6·7 and 8 per cent., and for hypothetical 'air' containing no argon at all, as treated in the last chapter. It is evident that $y_o - z_o$ is very much smaller in the presence of argon, especially in the lower part of the column. The points at which the curves begin to bend downwards correspond to the cross-sections of the column at which the argon accumulation is at its greatest. Below these points rectification takes place mainly between oxygen and argon, since the rectification curves in Fig. 132 are almost indistinguishable from the argon–oxygen side of the triangle. The small values of $y_o - z_o$ are therefore due to the proximity of the boiling- and dew-curves in the equilibrium diagram of the argon–oxygen system. They will require more plates than are needed in the case of a binary oxygen–nitrogen mixture.

Similar considerations should hold in a double column, but here the influence of the argon on the nitrogen must also be taken into account. Hausen finds theoretically an accumulation of argon in the lower section of the upper column up to concentrations of about 17 per cent. in the liquid and 21 per cent. in the vapour.

Still higher concentrations of 30–40 per cent. should occur, according to his theory in the upper section close above the feed plate. There is no record of such high argon contents having been found in practice above the feed of the upper column, and Fischer† concludes that there is no accumulation at this point. In air-separating plant from which an argon fraction is removed for further treatment, Ischkin and Bourbo‡ find experimentally below the feed of the upper column argon concentrations of 10 per cent. in the liquid and 14 per cent. in the vapour. Fig. 134 shows the composition of the vapour on the plates below the feed of an oxygen plant from which an argon fraction is withdrawn between the 16th and 17th plates from below.

2. The production of argon

Until recently the main application of argon was for filling incandescent lamps. As an inert gas with a high molecular weight it prevents

† V. Fischer, *Zeitschrift des Vereins Deutscher Ingenieure*. Beiheft 'Verfahrenstechnik', No. 3, p. 87 (1938).

‡ I. P. Ischkin and P. Z. Bourbo, *Journ. Techn. Phys.* (Russian), **9**, No. 18 (1939); *Kislorod*, **4**, No. 1, p. 14 (1947).

vaporization of the filaments and enables higher temperatures to be attained with a consequent increase in luminosity as compared with lamps filled with nitrogen. The light from argon lamps is 'whiter' than that from nitrogen lamps and more candle-power can be produced per watt input. Argon used for this purpose must be free of oxygen, but the presence of some nitrogen is desirable as it quenches luminous discharges. Most of the published work on argon production is therefore

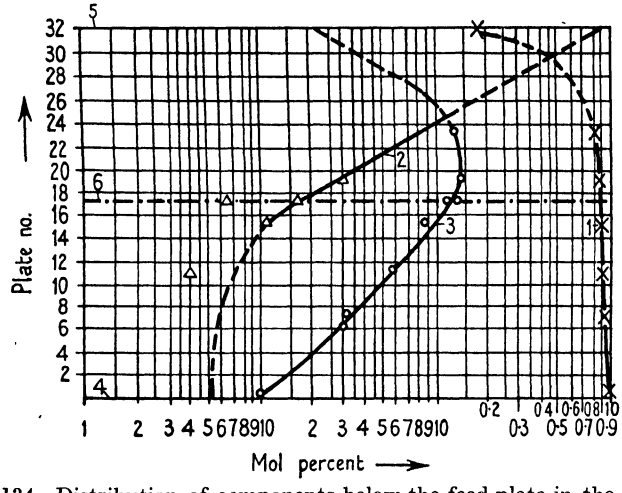


FIG. 134. Distribution of components below the feed-plate in the upper column of an oxygen plant from which an argon fraction is withdrawn
1. oxygen; 2. nitrogen; 3. argon; 4. bottom plate; 5 feed plate; 6. plate from which argon fraction is withdrawn

concerned with the supply of a 'technical argon' in conformity with this requirement.

In the last few years several new uses of argon have been found; in particular it is now needed as an inert atmosphere for an important arc-welding process. For this purpose pure argon is desirable and this is leading to some changes in the methods of argon production. In the following we shall deal only with the production of the 'technical argon' mentioned above.

It will be clear from the previous section that the production of argon is impossible without simultaneously producing fairly pure oxygen. At the same time the removal of some of the argon from an air column must have a beneficial effect on the production of pure oxygen.

Technical argon is obtained by withdrawing from the lower part of the upper air column an argon-enriched liquid or gaseous mixture, concentrating it in a separate argon column and removing the residual

oxygen chemically, as a rule by burning sulphur and scrubbing out the resulting SO_2.

Since the argon collects in that part of the air column in which the mixture has a high concentration of oxygen and a low nitrogen content, the function of the argon column must be to separate argon from oxygen. The crude argon thus appears as overhead from the argon column, which cannot therefore bring about a separation of nitrogen from argon. It is therefore necessary to withdraw argon-enriched mixture from a point in the air column at which the nitrogen content is sufficiently low to allow the final technical argon to contain less than 10 per cent. nitrogen. In practice the mixture fed to the argon column contains about 1 per cent. nitrogen and 7 or 11 per cent. argon depending on whether liquid or vapour is withdrawn from the air column.

Several types of argon plant have been used successfully, four of which are shown in Fig. 135. They differ mainly in the source of cold for providing reflux to the argon column. In some cases the feed to this column is liquid, in others it is gaseous.

To understand these flow diagrams, the three main problems of argon production must be appreciated. The first is to obtain as high a yield of argon as possible, the second is to keep down the cost of the argon, and the third is not to impair the quality and quantity of the oxygen product.

A high yield of argon means that both products of the air column must contain very little argon, and so the first and third problems are very closely linked. On the other hand a good separation of argon and oxygen in the argon column requires a very high reflux ratio, as may readily be inferred from the shape of the equilibrium curves in Fig. 32. This means either a high power consumption to supply the refrigeration needed for this reflux or the withdrawal of reflux from the air column in favour of the argon column, with a consequent tendency to lower the oxygen or nitrogen purity and hence lose argon. Even if we were prepared to tolerate this loss of argon, the effect would be to render the oxygen product valueless, at least for the engineering industry, where oxygen of 99·5 per cent. purity is required.

In the Linde oxygen–argon plant shown in Fig. 135*a*, a liquid fraction is withdrawn from the upper air column and fed to the argon column, which is equipped with a re-boiler as well as a reflux condenser. The reflux is provided by withdrawing gaseous nitrogen at 5·5 atm. abs. from the condenser-evaporator of the air column, condensing it in the re-boiler of the argon column, and evaporating it at atmospheric pressure in the reflux condenser.

The crude argon emitted as overhead from the argon column contains 45 per cent. argon, 50 per cent. oxygen, and 5 per cent. nitrogen. The argon yield is generally stated to be 30 per cent. This low yield is con-

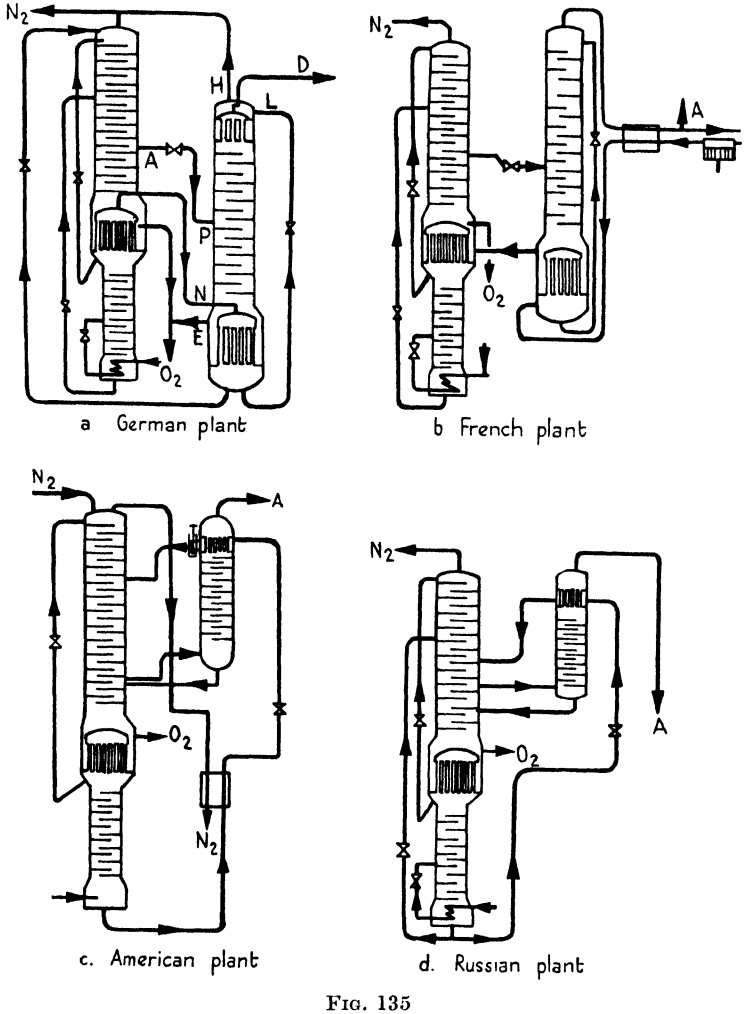


FIG. 135

sidered tolerable since no additional power is consumed for the production of argon over and above that needed to produce the oxygen and nitrogen.

The Claude plant shown in Fig. 135 *b* also uses a liquid argon fraction, but here the reflux in the argon column is obtained by re-compressing crude argon after warming it up in a heat-exchanger, condensing it in the re-boiler, and injecting the liquid at atmospheric pressure into the

top of the column. The additional power consumption is considerable, but the yield is much higher than in the Linde plant and the crude product contains 80–90 per cent. argon.

Fig. 135 *c* shows an American plant in which an argon-enriched vapour is fed to the argon column. This makes it possible to dispense with the re-boiler. Reflux is provided by the oxygen-enriched air from the bottom of the lower air column, which is sub-cooled in a heat-exchanger and expanded to atmospheric pressure before being fed to the condenser. Here a part evaporates and the vapour so formed, together with the remaining liquid, is introduced at the appropriate point of the upper air column. The liquid bottoms from the argon column are also returned to the air column.

This plant is provided with a Cascade refrigerating cycle which supplies liquid nitrogen to the top of the upper air column in addition to the reflux nitrogen introduced from the lower column. It is claimed that the argon column produces 90 per cent. argon with a yield of 80–90 per cent.

A Russian argon plant† shown in Fig. 135 *d* also introduces a gaseous mixture into the argon column and uses oxygen-enriched air to provide the reflux. Only so much liquid is supplied to the condenser as is actually required to evaporate, the rest being introduced into the upper air column in the usual way. No additional liquid nitrogen is fed to the air column and there is no cascade refrigerating cycle. The yield is given as 50 per cent. and the crude argon has a similar composition to that from the Linde plant.

Fischer‡ has calculated an argon column of the Linde type assuming that the liquid fraction withdrawn from the air column contains 11 per cent. argon and that the amount of nitrogen diverted from the air column is 25 per cent. of the total amount of air treated. Actually the argon content of the feed can hardly be more than 8 per cent. and not more nitrogen than is equivalent to 18 per cent. of the air treated can be withdrawn from the air column without impairing the purity of the oxygen. Thus Fischer's numerical results are somewhat optimistic, and the argon yields calculated are higher than those obtained in practice. Nevertheless, the example shows how the fundamental points of the argon column can be obtained. In the following the letters refer to Fig. 135 *a* and the compositions are given in weight per cent.

† M. B. Stolper, *Kislorod*, **4**, No. 1, p. 20 (1947).

‡ V. Fischer, *Zeitschrift des Vereins Deutscher Ingenieure*. Beiheft 'Verfahrenstechnik', No. 3, p. 87 (1938).

The amount m_P of argon fraction per pound of air will depend on the 'argon yield' of the primary column, i.e. on how much argon is lost with the oxygen and nitrogen products. Altogether there is 0·013 lb. of argon in every pound of air. If the argon yield of the primary column were 100 per cent., m_P would be $0{\cdot}013 \times 100/11 = 0{\cdot}118$. In practice m_P is usually not much more than half this value. 0·25 lb. of nitrogen per pound of air is probably more than the maximum quantity of refrigerant available, without destroying the régime of the primary column.

The following table contains the 'fundamental points' of the argon column with the values of those variables that have been fixed *a priori*:

Point	m	x	h
P	..	11	5
D	..	..	..
E	..	0	50·4
N	0·25	N_2	56
L	0·25	N_2	14·7
H	0·25	N_2	53

In the table the oxygen leaving the argon column is taken as pure, as the fraction of a per cent. of argon it contains would have little influence on the subsequent discussion. The values of h are in calories per gramme and taken from existing diagrams. h_P is not very accurate.

Of the remaining four variables (h_D depends only on x_D and is therefore not counted as a variable) two may be chosen arbitrarily between certain limits, whereupon the rest are automatically fixed, as we shall now show.

The balance equation of the column as a whole, if all nitrogen condensed in the re-boiler is passed to the condenser, reads

$$P+q = D+E+H-N, \tag{8}$$

where q is the heat loss through the lagging. This may be written

$$P+q = D+E-Q_1+Q_2, \tag{9}$$

where Q_1 is the heat introduced into the evaporator and Q_2 the heat withdrawn from the condenser.

For the balance of weight and composition we thus have

$$m_P = m_D+m_E, \tag{10}$$

$$m_P x_P = m_D x_D+m_E x_E. \tag{11}$$

Substituting (10) in (11), we obtain

$$m_D = m_E \frac{x_P-x_E}{x_D-x_P}. \tag{12}$$

Thus, if we introduce the values already fixed and choose m_E and x_D, m_D may be determined from (12) and m_P from (10). For the argon yield we then have

$$\alpha = m_D x_D / 0{\cdot}013. \tag{13}$$

For example, if we put $m_E = 0{\cdot}05$ and $x_D = 60$ per cent., we obtain

$$m_D = 0{\cdot}05 \times 11/(60-11) = 0{\cdot}011,$$

$$m_P = 0{\cdot}05 + 0{\cdot}011 = 0{\cdot}061.$$

This gives $$\alpha = 0{\cdot}011 \times 60/0{\cdot}013 = 51 \text{ per cent.}$$

In fixing the values of the free variables, we must consider that a high yield of argon is profitable as well as a high argon concentration in the final product. Unfortunately these two conditions are irreconcilable. For, as equation (12) shows, a large value of x_D entails a small value of m_D, and this more than counterbalances x_D in equation (13). From (12) it is, however, clear that we can increase x_D without lowering m_D or α, if we simultaneously increase m_E. But there is a definite limit above which m_E cannot be raised, as the following argument shows.

Fig. 136 represents a rough (h, x) diagram of argon–oxygen mixtures at atmospheric pressure, obtained by putting the enthalpies of saturated liquid oxygen and argon equal to zero and neglecting the heats of mixing in both phases. In this case the liquid boundary line coincides with the axis of abscissae, and the vapour curve is a straight line joining two points on the ordinate axes that mark off the heats of evaporation λ_o and λ_a of oxygen and argon respectively. The former is 50·4 cal. per gm., the latter 38·0 cal. per gm. The connodals are taken from the equilibrium curves, as determined by Bourbo and Ischkin.

The liquid argon fraction, containing 11 per cent. A, is expanded from 1·4 to 1·0 atm. abs. before it enters the column. This causes some liquid to evaporate and reduces the argon content of the liquid to about 9 per cent., which, when the column is properly adjusted, is equal to the argon concentration on the first plate below the entry. Point P' in Fig. 136 gives the position of this liquid on the boundary line.

Now, as was proved in Chapter IV, there is a point Z on the (h, x) diagram such that $L - G = Z$, if L and G denote liquid and gas in contact on any horizontal section of the column below the point of entry, and the number of plates required in this part of the column is obtained by joining the liquid ends of the connodals to Z and producing to the vapour curve. Moreover, it was shown that the column will not

function unless the straight line $P'Z$ is steeper than the connodal through P'. Z', where the projection of the connodal through P' cuts the oxygen axis, is therefore the highest value that Z can have when

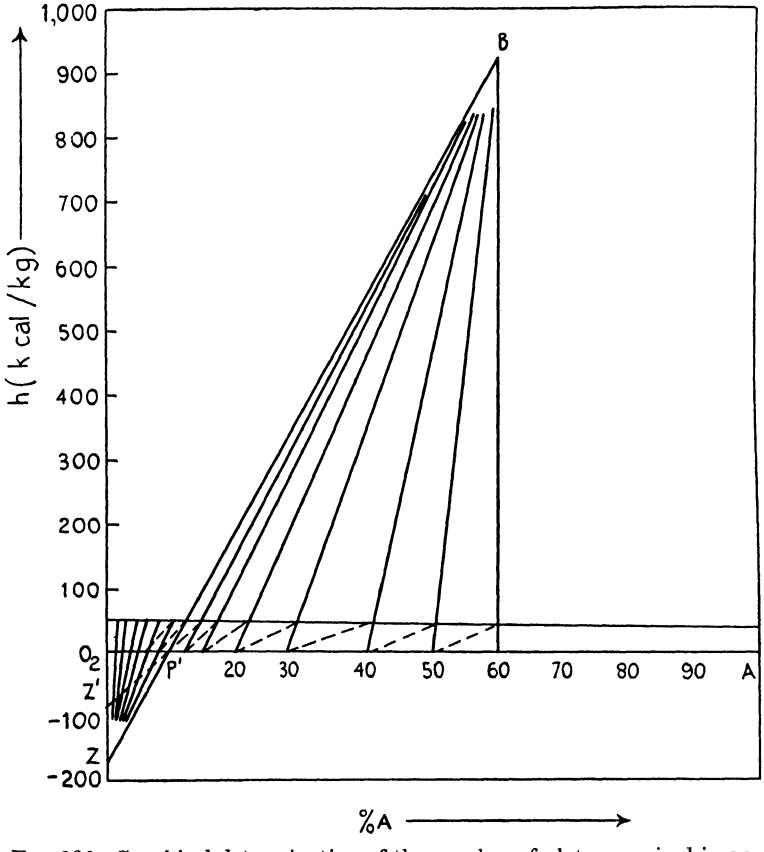


FIG. 136. Graphical determination of the number of plates required in an argon column on the (h, x) diagram of oxygen–argon mixtures

pure oxygen is to be obtained. We find $h_{Z'} = -82$ cal. per gm. Now the balance equation of the lower part of the column reads

$$L-G = E-Q_1 = Z, \tag{14}$$

which means

$$h_Z = h_E - Q_1/m_E, \tag{15}$$

$$Q_1 = m_N \lambda_{N_2},$$

where λ_{N_2} is the latent heat of evaporation of nitrogen at 5·5 atm. and is equal to 41·3 cal. per gm. Since $m_N = 0{\cdot}25$, we have

$$Q_1 = 0{\cdot}25 \times 41{\cdot}3 = 10{\cdot}3 \text{ cal.}$$

With $h_E = 50{\cdot}4$ cal., equation (15) gives

$$h_Z = 50{\cdot}4 - 10{\cdot}3/m_E. \tag{16}$$

From the above it is apparent that only those values of m_E are permissible for which $h_Z \leqslant -82$ cal. This gives

$$m_E \leqslant 0{\cdot}078 \text{ gm.}$$

It should be noted that this limiting value is independent of x_D and depends only on x_P. Thus $m_E = 0{\cdot}078$ gives us the maximum yield for any value of x_D.

With the help of equations (10), (12), and (13) we obtain the following values of α for various values of x_D and m_E. x_P is always taken as 11 per cent. and $m_V = 0{\cdot}25$ cal.

TABLE 23. *Argon Yield α in per cent. as a Function of Argon Concentration of Product x_D and Amount of Oxygen m_E emitted at Base of Column*

x_D \ m_E	0·05	0·06	0·07	0·078
50	56	67	78	87
60	51	61	71	79
70	50	60	70	78
80	49	59	69	77
90	48	58	68	75

Though an increase of m_E within permissible limits considerably raises the argon yield without lowering the concentration of the product, it has the effect of increasing the number of plates required. From Fig. 136 it is clear that $m_E = 0{\cdot}078$, which leads to $h_Z = -82$, entails an infinite number of plates in the argon column. The values in the last column of Table 23 are therefore fictitious. But even values of m_E in the vicinity of 0·078 lead to a large number of plates, in view of the proximity of liquid and vapour curves on the equilibrium diagram of oxygen and argon.

For $m_E = 0{\cdot}05$ and $x_D = 60$ per cent., Fischer showed that fifteen plates are theoretically sufficient if we allow 0·5 per cent. A in the oxygen product ($x_E = 0{\cdot}5$). Assuming a plate efficiency of about 70 per cent., we should need twenty-two plates in practice. Fig. 136 shows how the number of plates was determined.

If we turn once again to equation (9) we can compute Q_2 from h_H and h_L and find $Q_2 = 9{\cdot}6$ cal. Since $Q_1 = 10{\cdot}3$ cal., we see that more heat is supplied to the evaporator than is withdrawn from the condenser. So the nitrogen in the argon column does not act as a refrigerant

in the ordinary sense of the word, except in so far as it maintains the temperature head between top and bottom of the column. Taken as a whole, it supplies more heat than it withdraws.

3. Neon and helium

When a double air column works for long periods at a stretch it is generally found that the efficiency of the condenser-evaporator begins to fall off. The impression made is that the heat transfer between condensing vapour in the tubes and evaporating liquid around them deteriorates. This is due to the formation of an uncondensable cushion of gas, first in the dome above the condenser and finally in the tubes of the condenser itself. This gas is mainly nitrogen, but the gradual accumulation of neon and helium has so far lowered the partial pressure of the nitrogen that the existing pressure and temperature are insufficient to condense it. This effect is enhanced by the insufficiently rapid diffusion of neon and helium away from the walls of the tubes, where it becomes concentrated owing to the condensation of nitrogen.

This disturbing influence of neon and helium, which are themselves uncondensable under the operating conditions, is easily eliminated by blowing off the contents of the condenser at intervals through a purge line attached to the top of the dome. Thus the effect of neon and helium on the production of oxygen and nitrogen is much less pronounced than that of argon. This is due partly to the low concentration of these gases in atmospheric air (see Table 1) and partly to the fact that their boiling-points are much lower than those of both oxygen and nitrogen and not, as that of argon, between the two. Yet since the condenser is normally closed at the top, all the neon and helium passing through the plant, except for the very small traces that dissolve in the liquid nitrogen, must accumulate in the condenser and gradually fill it, if it is not removed.

The brilliant red light emitted by neon discharge tubes has created a demand for the gas in recent years, mainly for advertising purposes. Some air separators are therefore fitted out with auxiliary equipment for extracting a neon–helium fraction instead of merely blowing it off to the atmosphere.

The gas collecting in the condenser has a very low concentration of neon and helium, at any rate if it is blown off frequently enough to secure the proper functioning of the air column. But a simple device enables the neon and helium to be concentrated. The pressure in the condenser tubes is about 5 atm. and the temperature about 93° K.,

whereas the temperature at the top of the upper column is 78° K. If we introduce a small additional condenser at the top of the column and pass a small current of gas from the dome of the main condenser through it at 5 atm. pressure, a considerable portion of the nitrogen in this gas will condense and the neon–helium fraction will become richer. The composition of the final neon–helium fraction varies somewhat, but the average figures are roughly as follows:

TABLE 24. *Composition of Neon–Helium Fraction, per cent. by volume*

N_2 . . .	70 per cent.
Ne . . .	23 „
He . . .	7 „

The nitrogen can easily be removed by compressing the mixture to some 50 atm. and passing through a dephlegmator surrounded by liquid air or liquid nitrogen. The remaining traces of nitrogen can be adsorbed on charcoal at liquid air temperature, or, if this entails too great a loss of neon, absorbed on hot calcium or magnesium. It is important to remove all nitrogen from the mixture, as its presence destroys the colour and brilliancy of the discharge. On the other hand, helium has very little effect on the discharge, and 'technical neon', containing about 30 per cent. He is frequently employed in discharge tubes.

The separation of neon from helium is difficult and expensive, since neither can be condensed at temperatures attainable with liquid air or liquid nitrogen, the stock refrigerants of the low-temperature engineer. The lowest temperature attainable with liquid nitrogen is the triple point, 63° K., at which the vapour pressure is 9 cm. of mercury, a pressure difficult to maintain in a technical plant. But the critical temperature of neon is 42° K. and that of helium 5·2° K. To separate neon and helium, we must either employ a refrigerant colder than nitrogen or have recourse to other methods.

Theoretically, the most economic way to separate these gases would be to pass a compressed neon–helium mixture through a condenser cooled with liquid neon. The neon could be liquefied with the help of liquid air in a plant of the Linde type. But at present pure neon is not available in sufficiently large quantities to be used as a refrigerant, and the unavoidable losses in compressors and pipe-lines would be prohibitive.

Meissner† succeeded in separating some thousand cubic feet of neon–

† W. Meissner and K. Steiner, *Zeitschr. f. d. gesamte Kälteindustrie*, **39**, 49 and 75 (1932).

helium mixture with the help of liquid hydrogen, in order to obtain helium for laboratory purposes. His plant, which was on a semi-technical scale, was built at the Physikalisch-technische Reichsanstalt at Charlottenburg. The laboratory had a large plant for producing about 12 litres of liquid hydrogen per hour by the Linde method, and this plant was so well constructed that only 1 litre of liquid nitrogen was needed for each litre of liquid hydrogen produced. Liquid hydrogen was therefore a comparatively cheap refrigerant. The neon–helium mixture, slightly above atmospheric pressure, was passed through a condenser cooled with liquid hydrogen. The neon was thus condensed, and the helium, with very small admixtures of neon, remained in the gaseous state. The remnants of neon were removed with active carbon.

The boiling-point of hydrogen is 20·4° K. and that of neon 27·2° K. There is thus no difficulty in condensing the neon in liquid hydrogen. However, the triple point of neon lies at 24·6° K., above the boiling-point of hydrogen. Precautions have therefore to be taken to prevent the neon from solidifying and blocking the tubes. This difficulty can be eliminated by maintaining the pressure above the liquid hydrogen at 3 atm., which suffices to raise its boiling-point above the triple point of neon.

Small quantities of neon and helium may be separated very effectively by fractional sorption on charcoal at low pressures and liquid-air temperatures. An elegant method for doing this has recently been developed by Glückauf. By a suitable arrangement of sorption tubes and mercury cut-offs a complete separation can be effected in a couple of hours.

From the industrial point of view, the separation of neon and helium is of interest only for producing neon. Helium obtained from air is far too expensive to compete with the cheap helium produced from natural gas, as will be described in Chapter XI.

4. Krypton and xenon

Since the boiling-points of the heavy rare gases, krypton and xenon, are higher than those of all the other constituents of atmospheric air, these substances will naturally tend to accumulate in those parts of a separating plant that show the highest oxygen concentrations. Since oxygen is easily removed by chemical means, small quantities of mixtures may be obtained, consisting mainly of argon and nitrogen, but containing quite appreciable traces of krypton and xenon. By a series of arduous small-scale processes the heavy rare gases can then be separated from the other components and ultimately from each other.

This laboratory technique was fairly satisfactory as long as krypton and xenon were needed only for scientific experiments. But it became hopelessly inadequate as soon as large quantities of these gases were required for industrial purposes.

The issue was raised on a completely new level when it was suggested that krypton and xenon could advantageously replace argon for the filling of incandescent bulbs. Their high atomic weight reduced vaporization of the filaments very considerably, allowing higher temperatures to be used in the lamp with a corresponding increase in efficiency, and their low thermal conductivity made it possible to reduce the size of the bulbs. The advantage is particularly marked for smaller bulb sizes, and it is generally held that bulbs of less than 100 watt should be filled with krypton and the larger sizes with argon. The Russians estimate their krypton requirement in 1950 at 4,000 cu. m. per annum. To satisfy this demand, it would be necessary to treat about 600,000 cu. m. of air per hour, which is roughly the capacity of 30 Linde–Fränkl plants each making 3,500 cu. m. of oxygen per hour.

In addition to its use in incandescent bulbs, krypton is a very suitable gas for filling discharge lamps as, with a certain amount of blending, it gives the effect of daylight. It is also required for some intensive forms of cinema lighting and for filling various appliances of the electro-vacuum industry.

For all these applications the presence of xenon in the gas is permissible and the term 'krypton' is generally used to denote a mixture containing rather over 90 per cent. krypton and rather less than 10 per cent. xenon. In the following the word will be used in this sense.

To separate from air on a commercial scale a gas contained in it with a concentration of one part in a million is a formidable task. The most natural way to set about it is to regard krypton, like argon, as a by-product of oxygen and to devise subsidiary equipment, to be used in conjunction with existing oxygen plant, for the production and purification of a 'krypton fraction'. One of the many early difficulties of this method was the small amount of krypton that could be produced even from relatively large oxygen plants. Thus, a combined oxygen–krypton unit with a capacity of 1,000 cu. m. per hour of oxygen could, even with a hundred per cent. krypton yield, not deliver more than 40 cu. m. of krypton per annum. In addition to this, the krypton yield of most of these plants was found to be unexpectedly low.

Under these circumstances, a number of firms, in particular the Air Liquide Company, began to design plants expressly for the production

of a krypton–xenon mixture from air, without any separation of the major components.

Ordinary air-separating plant requires about 5 atm. pressure in the main cycle and an auxiliary high-pressure cycle for about 10 per cent. of the air circulated. The 5 atm. are essential to enable all the air to be liquefied in the course of the cycle, after which it is again evaporated. All rectifying plants contain this as an important feature. But it would be far too expensive to compress all the air to 5 atm., not to mention the high-pressure cycle itself. A process was therefore sought which did not require the liquefaction of all the air in the course of the cycle, but which would enable the krypton to be extracted from the air without liquefying more than a small portion of it. The problem was solved by the Air Liquide Co. by the development of a new type of scrubbing process.

The essential feature of this process is that a large quantity of gaseous air is scrubbed in countercurrent by a small quantity of liquid air, as a result of which almost all the krypton is removed from the gas and dissolved in the liquid. The krypton content of the large quantity of gas is thus transferred to the small quantity of liquid, giving a rich krypton mixture, which is further enriched in the plant by partial evaporation and rectification. In this way it is possible to remove almost all the krypton from air at a pressure of only 1·7 atm. abs., only about 5 per cent. being compressed further to 15 atm.

The plant envisaged in Claude's original patent† (1933–5) is sketched in Fig. 137. The air, compressed to 1·7 atm. abs. and not previously purified, is cooled in one of the alternating regenerators A, A' and expanded in the turbine T, which it leaves as a saturated vapour at $-190°$ C. It is then admitted at the bottom of the upper portion B of a rectifying column, where it is scrubbed with a small quantity of liquid air, from which the krypton has already been removed. This scrubbing liquid is obtained by withdrawing a small portion of the air at the top of the column, warming it up to room-temperature in the heat-exchanger E, and compressing it to 15 atm. in the compressor C. The compressed air is thereupon cooled again in E and expanded to 2 atm. in the expansion engine H. It is then liquefied in the evaporator at the bottom of the lower column B', expanded to atmospheric pressure in the valve V, and delivered at the summit of B. After traversing B, the liquid, which now holds all the krypton formerly contained in the much larger quantity of air, is further enriched in the lower column

† British Patent 432,644.

B'. The unevaporated liquid residue is delivered from the evaporator of B' to the summit of the subsidiary column D, in which the krypton concentration is raised further. The final purification is effected by other methods, which will be discussed later.

In a subsequent patent† (1936–7) the Air Liquide Co. developed the scrubbing process so as to combine it with nitrogen production, thus returning to a certain extent to the original idea of producing krypton

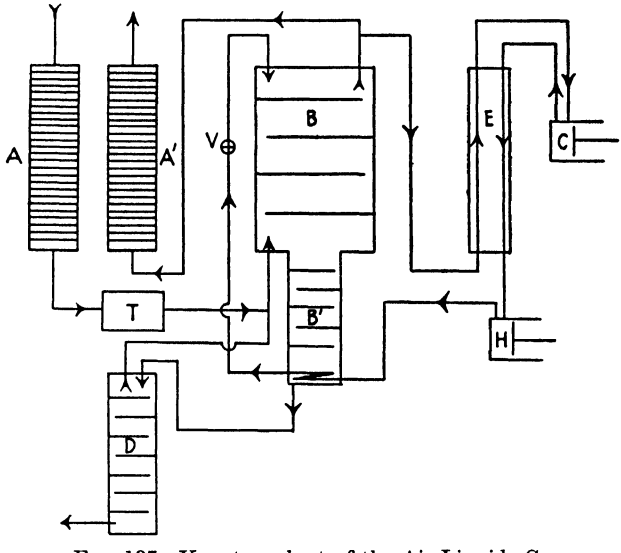


FIG. 137. Krypton plant of the Air Liquide Co.

as a by-product of the air-separating industry. But the alteration in existing air plant, as here suggested, is very much more radical than would have been deemed necessary a few years earlier, and it would be more accurate to regard this new process as a way of making air separation a subsidiary process of the krypton industry.

The krypton scrubbing process may be combined with any of the standard methods of air separation. Fig. 138 shows how it can be used in conjunction with the two-column rectifying plant. The upper column B, working at atmospheric pressure, has a wide section B', fitted with a small number of the usual plates. A quantity of atmospheric air, which can be twenty times as great as the amount separated in the column, is admitted at I at the bottom of B', scrubbed with liquid nitrogen and liquid air taken from the lower column A, and withdrawn at K, after giving up all its krypton to the liquid. A liquid fraction,

† British Patent 468,872.

containing most of the krypton, is removed at L at the bottom of B, and fairly pure oxygen vapour, containing some of the krypton, is withdrawn at F. One or both of these fractions can be further treated for krypton. The air to be separated in the two columns is introduced as usual at the bottom of the lower column A at a pressure of some 4 atm. As the reflux in B is sufficient to produce more nitrogen than it contains itself, the amount of air withdrawn at K can be smaller than that admitted at I. The production of krypton is thus combined with an increased production of nitrogen in the air column.

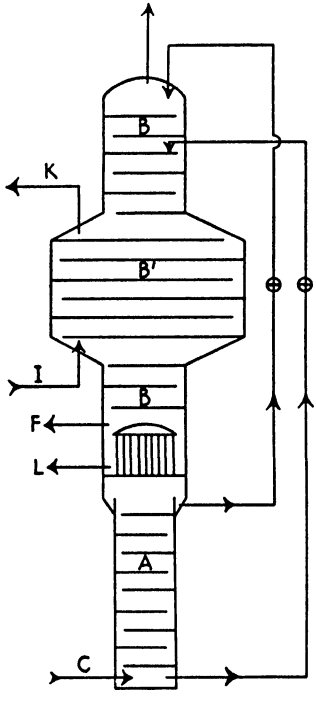


FIG. 138. Double column for krypton and nitrogen

The efficiency of the scrubbing process depends to a great extent on the vapour pressure of the krypton at the scrubbing temperature. It is therefore important to scrub the air with as cold a liquid as possible. The vapour pressure of pure krypton is 90 mm. at 90° K. and only 4 mm. at 80° K. It is therefore much more economical to scrub with liquid air than with liquid oxygen.

There are thus in operation essentially three types of plant for effecting an initial concentration of krypton and xenon from atmospheric air:

1. Standard air-separating plants with subsidiary equipment for concentrating krypton in liquid oxygen.
2. Plants for producing only krypton directly from air.
3. Specially designed combinations, differing in some important aspect from conventional air-separating plants, for producing krypton simultaneously with one or both of the major components.

In all cases the result is a 'lean' krypton fraction containing from 0·1 to 0·2 per cent. krypton–xenon mixture in fairly pure oxygen. It is not considered advisable to go beyond this concentration in the first series of steps because of the explosion hazard caused by the presence in the atmosphere, especially in industrial areas, of acetylene and other hydrocarbons. In such districts the air has been found to contain up to $2\text{–}8 \times 10^{-4}$ per cent. of acetylene by weight, as compared with 3×10^{-4}

per cent. by weight of krypton. It is essential to remove this while it is still in a dilute solution with oxygen, and this is done by withdrawing the lean krypton fraction, warming it up and passing it over a heated catalyst. After drying and removal of the CO_2 formed by burning the hydrocarbons, the krypton fraction is cooled down again and enriched

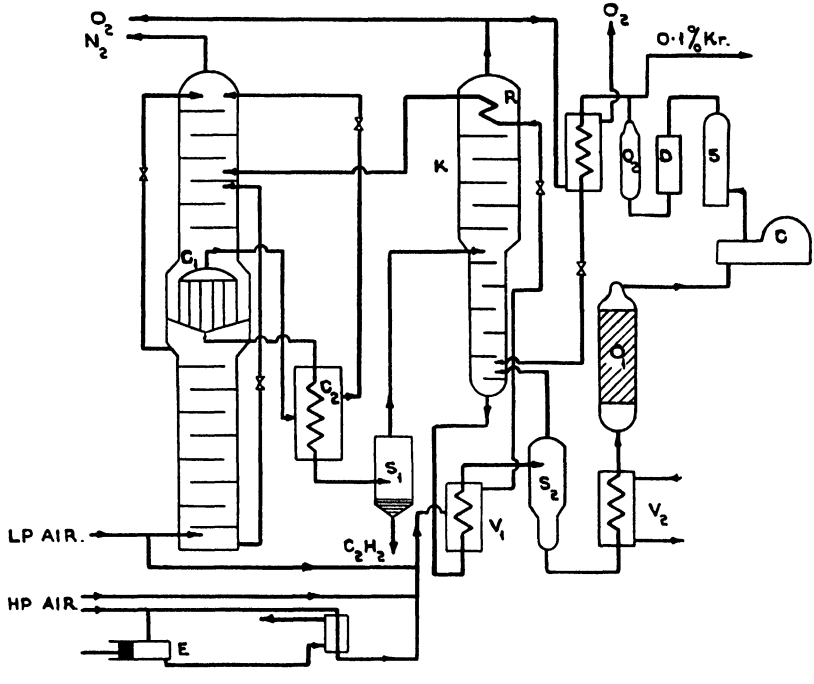


FIG. 139. Leuna oxygen–krypton plant

in further rectifying columns. In general the krypton–xenon concentration is raised to 30–40 per cent. in one further stage and to 98–99 per cent. in a final column. Even in the largest commercial plants, all equipment after the primary enrichment section is quite small and on a laboratory scale.

As an example of a standard air-separating plant with subsidiary krypton equipment, Fig. 139 shows schematically one of the oxygen–krypton units installed by the Linde Co. at Leuna.† This was a Linde–Fränkl plant producing 2,800 m.^{3} per hour of 98 per cent. oxygen, together with an 80 per cent. krypton–xenon mixture amounting to 10 L/hr. with an overall krypton recovery of about 50 per cent.

A stream of liquid oxygen from the condenser-evaporator C_1 of the

† *BIOS Report*, No. 591, Item 30.

main air column is largely evaporated in the external condenser C_2, a small quantity containing almost all the acetylene being withdrawn as a liquid from the bottom of the separator S_1. Evaporation of the oxygen in C_2 serves to condense nitrogen which passes as a gas to C_2 from the dome of C_1. This liquefied nitrogen is fed to the top of the upper air column along with the nitrogen transferred from the lower column. The evaporated oxygen, which contains most of the krypton from the original air, is introduced into the bottom of the upper section of the first krypton column K. Most of the liquid from the bottom of this column is evaporated in the vaporizer V_1 and returns through the krypton separator S_2 to the column. The liquid krypton concentrate passes from the bottom of S_2 through the vaporizer V_2 and the copper oxide tower O_1 to a compressor C. Compressed to 5 atm. abs., the lean krypton stream traverses a scrubber S for the removal of CO_2, a dryer D and a further copper oxide furnace O_2, after which a part returns to the bottom of the krypton column K and the rest is further concentrated in equipment not shown in the figure.

High-pressure air, precooled in an exchanger with a portion expanded in a reciprocating engine E, is further cooled in V_1, expanded to low pressure in a valve, and the liquid so formed is evaporated in the reflux condenser R of column K. It is then admitted as 'Lachmann air' to the middle of the upper air column.

This particular plant, which was built before 1940, is limited to the production of oxygen and krypton. In a later variant erected in 1942 pure nitrogen was produced also, some air, containing most of the argon, being withdrawn at an intermediate point of the upper air column.

Several large plants have been built for the extraction of krypton–xenon mixtures alone from atmospheric air, using a combination of scrubbing towers and rectifying columns. One unit erected at Boulogne by the Air Liquide Co. treats 33,000 m.^{3} of air per hour. Another built by the Linde Co. in Hungary treats 25,000 m.^{3} per hour, extracting 200 m.^{3} of pure krypton–xenon mixture containing 93·5 per cent. krypton and 6·5 per cent. xenon. The krypton recovery is very high, amounting to just over 90 per cent. The power consumption is 34–36 kWh for 1 litre of product.

The latter plant, which has been described by Fastovsky,† is very complicated, in particular the cycles supplying liquid air to the scrubbers and refrigeration for reflux in the rectifying columns. Three different air pressures are used involving rotary and reciprocating compressors,

† V. G. Fastovsky, *Kislorod*, **4**, No. 1, p. 5 (1947).

an expansion turbine and a reciprocating expansion engine, as well as two pairs of alternating regenerators.

A combined unit for the production of technical oxygen and a krypton–xenon concentrate was recently designed by Fastovsky.† Though this plant is not yet known to be in operation, it is of interest in that it is the only krypton plant of which a full calculation has been published.

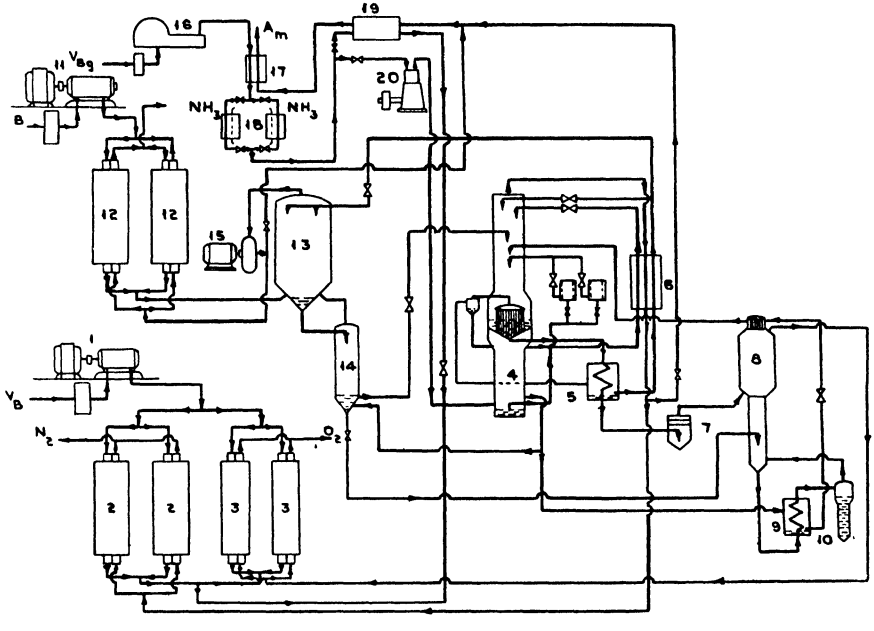


FIG. 140. Proposed Russian krypton plant

The oxygen unit is of the Linde–Fränkl type, but krypton is extracted not only from the oxygen product, but also from a larger quantity of low-pressure air, which is not further separated. For this purpose that portion of the nitrogen from the Linde–Fränkl plant which is customarily fed to the expansion turbine is withdrawn as liquid and made to scrub the additional air. The cold so lost is made up by increasing the high-pressure cycle.

It will be clear from the flow sheet shown in Fig. 140 that the krypton column 8 is fed from two sources: a vapour stream comes from the oxygen produced in the air column 4 by way of the external condenser 5 and the separator 7; and a liquid stream introduced from the subsidiary column 14, originates in the air scrubber 13. The amount of additional

† V. G. Fastovsky, Y. V. Petrovsky, and M. B. Stolper, ibid. No. 6, p. 22 (1947).

air treated in the scrubber is about 4 times the quantity separated in the Linde–Fränkl plant. It is compressed to 1·7 atm. abs. in the turbo-blower 11 and, after extraction of the krypton, expanded to 1·15 atm. in the turbine 15. The ratio of liquid to vapour in the scrubbing tower is 0·05 and the krypton product contains 0·2 per cent. krypton. The overall krypton recovery is taken as 81 per cent. and the additional power requirements for krypton over and above the usual consumption for oxygen production in the Linde–Fränkl plant are found to be 21·8 kWh per litre.

X

THE PRODUCTION OF HYDROGEN FROM COKE-OVEN GAS

1. Separation by partial condensation

COKE-OVEN gas is one of the principal sources of industrial hydrogen. At the present state of industrial development, hydrogen from coke-oven gas is rather more expensive than hydrogen from water gas, but much cheaper than electrolytic hydrogen. The separation of water gas is effected by chemical means, the carbon monoxide being converted to carbon dioxide and then absorbed. A low-temperature method invented by Frank and Cario is now obsolete. We shall therefore not discuss the production of hydrogen from water gas.

The methods evolved for separating coke-oven gas by partial condensation and rectification at low temperatures, though by no means completely satisfactory, have been developed to a considerable degree of perfection, and have given rise to standard plants designed on a very large scale. The units constructed in Germany and the U.S.S.R. separate some 200,000 cu. ft. of gas per hour.

The aim of coke-oven gas separation is to produce hydrogen. For hydrogenation purposes the hydrogen should be as pure as possible; for the synthesis of ammonia a mixture is required containing 75 per cent. by volume H_2 and 25 per cent. N_2. Adulteration with nitrogen is therefore not only permissible but even desirable. On the other hand, the catalysts on which the ammonia synthesis is effected are poisoned by very small traces of carbon monoxide or oxygen. It is therefore important that neither of these gases should be present in the final product. Since the boiling-points of nitrogen and carbon monoxide are only 6° apart, it is difficult to separate a product containing N_2 but no CO. In practice the other constituents of coke-oven gas, such as methane and ethylene, are not produced in anything like a pure state, but emerge in the form of several fractions, each containing two or more constituents. These fractions are often subsequently reunited and form a gas of high calorific value, usually known as rich gas.

The problem of separating coke-oven gas differs very considerably from that of separating air for the following reasons:

1. Whereas air is essentially a mixture of two components with comparatively slight impurities, coke-oven gas, as is shown in Table 3, p. 3, contains at least six constituents with concentrations over 1 per cent.

2. Apart from the constituents listed in Table 3, crude coke-oven gas contains a number of other components, which are usually removed before the gas enters the low-temperature unit. These are not only water and carbon dioxide, which occur in air also, but considerable quantities of naphthalene, benzene, toluene and xylene, ammonia, nitric oxide, and several sulphur compounds. These constituents require special treatment.
3. Whereas the boiling-points of nitrogen and oxygen, the principal constituents of atmospheric air, are only 13° apart, and the condensation of one is impossible without the other, about half the coke-oven gas consists of hydrogen, which is still in the gaseous state when all the other constituents are already liquid. Since hydrogen is the principal product, rectification is in this case unnecessary and the process can be based on partial condensation.

The separation of a binary mixture by partial condensation was illustrated in Chapter III for the case of nitrogen and helium. It was shown that these two gases may be separated very effectively by this method. Now coke-oven gas, as we have seen, is not even approximately a binary mixture; nevertheless, some important points can be made clear by considering a binary model, consisting of the two principal components of coke-oven gas: hydrogen and methane. Following an example given by Hausen,† we shall consider a mixture, consisting of 70 per cent. H_2 and 30 per cent. CH_4 at 8 atm. pressure, which is to be separated by partial condensation. To simplify matters still further, we shall assume that no hydrogen dissolves in liquid methane. This is not strictly true, as may be seen from Fig. 40 on p. 53, but that is immaterial for the points we are discussing.

As in our example in Chapter III, methane will begin to condense at a temperature at which the pressure of its saturated vapour π_c is equal to the partial pressure p_c of methane in the mixture. As the total pressure p is 8 atm., and the methane concentration is 30 per cent., the partial pressure of methane before condensation commences is 2·4 atm. This is the vapour pressure of pure methane at −150° C. But only a drop of methane will condense at this temperature; for as soon as condensation begins, the partial pressure of methane in the gas will drop below 2·4 atm., and the temperature will have to be lowered further in order that condensation may continue.

Let m_c be the number of moles of methane in the original mixture

† H. Hausen, *Geschichte der Gesellschaft für Linde's Eismaschinen*, Wiesbaden, 1929, p. 155.

nd $m-m_c$ the number of moles of hydrogen, and at a given tempera-ıre suppose that m_l moles of methane have condensed. Then, if we ssume that the gas laws are valid in the vapour,

$$\frac{m_c-m_l}{m-m_c} = \frac{p_c}{p-p_c};$$

'hence

$$m_l = m_c - \frac{p_c(m-m_c)}{p-p_c},$$

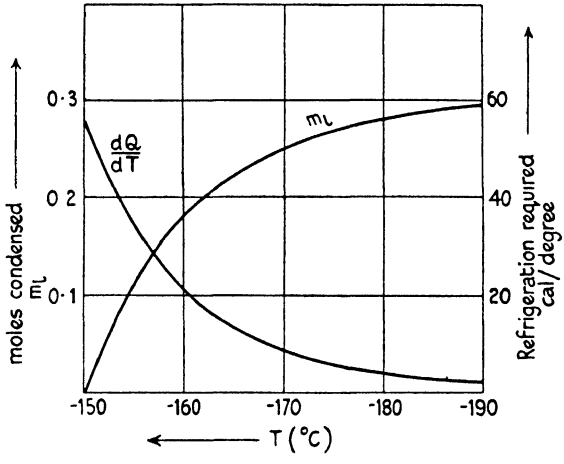


FIG. 141. Condensation of methane from a mixture containing 70 per cent. H_2 and 30 per cent. CH_4 at 8 atm.

r, since $p_c = \pi_c$,

$$m_l = m_c - \frac{\pi_c}{p-\pi_c}(m-m_c).$$

f 1 mole of gas was present to begin with, we have

$$m_l = 0{\cdot}3 - \frac{0{\cdot}7\pi_c}{8-\pi_c}.$$

Knowing the vapour pressure of methane as a function of temperature, ve can thus calculate the amount of methane condensed as the tem-ıerature is lowered.

The result of this calculation is shown in Fig. 141. We see that the urve giving m_l as a function of T rises steeply at first as the tempera-ure falls, but becomes gradually flatter. At $-161°$, the boiling-point f methane at atmospheric pressure, about 0·18 moles, or 60 per cent., f the methane has been condensed. But even at $-180°$ only 0·285 noles, or 95 per cent., is liquid. Five per cent. of the methane is still n the vapour phase, which now contains 98 per cent. H_2 and 2 per ent. CH_4. Evidently hydrogen and methane can be separated quite

efficiently by this method, but we must cool to very low temperatures in order to bring about anything like a complete separation. Condensation of methane takes place along a very great interval of temperature.

But this is only one of the facts which this example shows. Another concerns the refrigeration that we must supply to carry out the process. As long as the gases are merely being cooled, the heat that must be withdrawn from them for each degree through which their temperature is lowered is equal to their heat capacity. The specific heat of hydrogen at constant pressure in this temperature interval is about 7 cal./mole °C.; that of methane about 10 cal./mole °C. The total heat capacity of the mixture is therefore about 8 cal./mole °C. The refrigeration needed to withdraw this heat is usually supplied by allowing a colder gas to exchange heat with the gas that is being cooled. But as soon as liquefaction sets in, latent heat of condensation must be withdrawn, and a stream of cold gas seldom has a sufficient heat capacity to absorb this heat. A pure gas, or a mixture of two gases with boiling-points close to one another, condenses at a certain temperature or in a narrow temperature interval, and the heat of condensation can be absorbed by causing a second liquid to evaporate. But in the case of our hydrogen–methane mixture, the latent heat to be withdrawn is spread out over a long range of temperature. It is therefore much more difficult to find a suitable refrigerant.

Let us consider this problem from the quantitative side. We shall call the latent heat of evaporation of methane λ (cal./mole) and assume, as is approximately the case, that λ is independent of whether or not the vapour is mixed with hydrogen. Then for each infinitesimal amount dm_l of methane condensed, an amount dQ of heat must be withdrawn such that

$$dQ = \lambda\, dm_l.$$

If dm_l is condensed by lowering the temperature by $-dT$, we have

$$dQ = -\lambda \frac{dm_l}{dT} dT.$$

But

$$m_l = m_c - \frac{\pi_c}{p-\pi_c}(m-m_c).$$

Therefore

$$dQ = (m-m_c)\lambda \frac{d}{dT}\left(\frac{\pi_c}{p-\pi_c}\right) dT,$$

or

$$dQ = \frac{(m-m_c)\lambda p}{(p-\pi_c)^2} \frac{d\pi_c}{dT} dT = \frac{(m-m_c)\lambda \pi_c p}{(p-\pi_c)^2} \frac{d \log \pi_c}{dT} dT.$$

But according to the Clausius–Clapeyron equation, when the vapour

is a perfect gas and its volume great compared with that of the liquid,

$$\frac{d\log\pi_c}{dT} = \frac{\lambda}{RT^2},$$

and we may write $$dQ = \frac{(m-m_c)\lambda^2 p\pi_c}{(p-\pi_c)^2 RT^2}\,dT.$$

In our example $m-m_c = 0{\cdot}7$ and $p = 8$ atm. The latent heat of methane is $\lambda = 2{,}000$ cal./mole, and R may be taken as 2 cal./mole deg. So we obtain

$$\frac{dQ}{dT} = \frac{0{\cdot}7\times 4\times 10^6\times 8\times\pi_c}{(8-\pi_c)^2\times 2\times T^2}$$

$$= \frac{11{\cdot}2\times 10^6\times\pi_c}{(8-\pi_c)^2\times T^2}.$$

Again using the known vapour-pressure curve of methane, we can now calculate dQ/dT as a function of T. In this way we obtain the second curve in Fig. 141, which shows us how much heat must be withdrawn from the hydrogen–methane mixture, over and above that needed to cool the gas, for each degree through which it is cooled during condensation. We see that this amount of heat is great at first, where condensation is rapid, and that it falls off at lower temperatures when most of the methane is condensed. The total area covered by the curve, $\int_{-150} (dQ/dT)\,dT$, must, of course, equal $0{\cdot}3\lambda$ or 667 cal. The upper limit of the integral should, strictly speaking, be the absolute zero of temperature; practically it will suffice to integrate down to about −200° C.

We see that, between −150 and −170°, the latent heat to be withdrawn is greater, initially indeed much greater, than the heat capacity of the gas, although λ is spread out over a large temperature interval. Moreover, this heat varies very sharply with the temperature. Clearly it would be difficult to use a stream of gas as a refrigerant to absorb this heat.

We are therefore faced with the necessity of using a boiling liquid to absorb the heat of condensation of the vapour, even when the latter, as in our example, condenses over a wide temperature interval, and it is customary to use a pure liquid as the refrigerant, the temperature of which remains constant during evaporation. Since the refrigerant must, of course, be colder than the substance which is being cooled, the boiling-point of the refrigerant must be lower than the lowest temperature needed to condense the methane. In our example, if less than 2 per cent. of the methane is to remain, the temperature of the refrigerant must be not higher than −190°, since a temperature head of at least 4° must be allowed to ensure a sufficiently rapid heat

exchange. The only refrigerant available at this temperature is liquid nitrogen, which boils at —196° C. at atmospheric pressure. To separate a mixture of hydrogen and methane it is thus necessary to use liquid nitrogen as a refrigerant, a substance whose normal boiling-point is very much lower than that of the methane itself.

This result can be generalized as follows. To separate a mixture of two substances with widely different boiling-points by almost complete condensation of one of the components, the mixture must be cooled well below the boiling-point of that component with the help of a liquid refrigerant whose boiling-point is lower than that of the component to be extracted.

This necessity is fraught with two very serious disadvantages. Firstly, according to Trouton's rule, the heat of evaporation of a substance is the greater the higher its boiling-point. Therefore, to condense a substance by evaporating a refrigerant of a lower boiling-point, we need more of that refrigerant than the amount of substance actually condensed. For example, the heat of evaporation of methane is 2,000 cal./mole, that of nitrogen only 1,336 cal./mole. In order to condense 1 mole of methane we must therefore evaporate 1·5 moles of nitrogen, even assuming that the heat withdrawn from the hydrogen is completely regained.

Moreover, by using liquid nitrogen to condense methane from a mixture, we must bring the nitrogen, boiling at —196°, into contact with the mixture at a very much higher temperature—in the example just quoted —150° C. We thus obtain an unnecessarily large temperature head of 46° C. between the ingoing mixture and the refrigerant. Except in so far as heat exchange is accelerated, this temperature head is wasted, since it leads to an increase in entropy of the system as a whole, without any work being done by the system, and the process becomes highly irreversible. This wasted entropy ΔS, as we saw in Chapter IV, necessitates the expenditure of an additional amount of work $T'\Delta S$, where T' is room-temperature, over and above the work that would be needed if the process were reversible. This additional 'irreversible work' appears as additional work of compressing the nitrogen to a higher pressure than would be necessary in a reversible process.

We see that, even in the simple case of separating a hydrogen–methane mixture, partial condensation gives rise to serious complications. These become much more marked in the case of a complex system like coke-oven gas, which consists of many components of different boiling-points. As the temperature of such a mixture is gradually lowered, one component after another begins to condense, usually dragging with it portions of other components which are

partially soluble in it. The temperature intervals in which condensation occurs will vary in extent and in position with the concentrations of the components and with the pressure of the mixture. At the same time, the heat to be withdrawn in a given interval of temperature will vary quite irregularly. In one interval, where a certain component is extracted, it may be very large, in the next interval it may be small, and in the next large again. If we were to plot as a function of temperature the enthalpy of the mixture at the particular pressure, we should obtain an irregular curve, and if we want to cover these refrigeration requirements as economically as possible, we must employ our refrigerants in such a way as to provide the necessary cold but maintain the temperature of the refrigerant closely below that of the mixture being separated. The curve showing the enthalpy of all our refrigerants together should therefore follow as closely as possible the curve representing the enthalpy of the mixture.

In practice it is usually impossible to achieve a very striking similarity between the two curves. All we can really do is to achieve a balance of heat, while the temperature heads between mixture and refrigerants will be large at one point and small at another. Very much depends on the skill of the designer and on the amount of data available, which is as yet by no means complete.

2. The Linde-Bronn process

The considerations of the preceding section lead naturally to a process for separating coke-oven gas, based on partial condensation and on the utilization of liquid nitrogen. The Linde-Bronn process, first applied in 1924, was devised with the object of producing a stoichiometric mixture for ammonia synthesis, containing 75 per cent. H_2 and 25 per cent. N_2. Great care is taken to remove all other constituents from the mixture, especially CO and O_2, but no attempt is made to obtain any other components in a state of purity. On the contrary, methane, ethylene, carbon monoxide, and considerable quantities of nitrogen leave the plant together in the form of 'rich gas'. As in all methods for separating industrial gases, the preliminary purification of the crude gas, before it enters the low-temperature unit, is complicated and voluminous. We shall first consider the gas as it leaves the purifying plant, free from moisture and carbon dioxide and containing no components with higher boiling-points than propylene.

The Linde-Bronn process was evolved by men who were experts in air separation according to the Linde methods. It has therefore

preserved several features of the Linde air-separating plant, which forms a part of it, including the extensive use of ammonia refrigeration.

The most important element in the Linde-Bronn process is the use made of nitrogen. In these plants nitrogen is employed for three distinct ends. Firstly, it supplies all the refrigeration required at temperatures below those obtainable with ammonia; secondly, it is used to scrub out the last traces of carbon monoxide from the final product, and thirdly, it is introduced into that product to bring about the correct stoichiometric composition for the synthesis of ammonia.

A large ammonia cycle usually serves to precool the air entering the nitrogen plant as well as the coke-oven gas entering the low-temperature unit. The ammonia is made to boil under reduced pressure at $-48°$ C., and both the nitrogen and the coke-oven gas enter the final separating plant at $-45°$ C. The coke-oven gas is maintained throughout at a pressure of about 13 atm. and the final product emerges at this pressure.

The low-temperature plant (Fig. 142) consists of a number of condensers and heat-exchangers embedded in lagging material within a single outer covering. The coke-oven gas first traverses three heat-exchangers, in which it is cooled by outgoing products. In the first, E_1, its temperature is lowered to $-100°$ C. and very little condensation takes place. Small quantities of liquid propylene and ethane with traces of dissolved ethylene collect in the sump of the exchanger and are blown off at intervals through a valve. In the second exchanger, E_2, which the gas traverses from below, a temperature of $-145°$ is attained, sufficiently low to condense the greater part of the ethylene, the remains of the ethane and propylene, and a little methane. As the total amount of liquid formed is relatively small, the cold gaseous products are all the refrigerant required. The liquid, which is called the *ethylene fraction*, collects partly in the sump of the exchanger, the rest being carried on by the gas and deposited in a trap, T. The gas thereupon passes through the third heat-exchanger, E_3, in which it is further cooled, more methane condensing. The temperature behind this exchanger is usually given as $-180°$ C. The refrigerants in the third exchanger are methane and a mixture of nitrogen and carbon monoxide. But, as we saw in the last section, liquid methane is not sufficiently cold to remove all the methane from the mixture. It must be supplemented by liquid nitrogen. The coke-oven gas, together with the liquid formed in the third exchanger, passes up through the tubes of a condenser C surrounded by liquid nitrogen boiling under atmospheric pressure. It is here cooled to about $-190°$ C. and almost all the

methane is condensed, together with the rest of the ethylene, some oxygen, carbon monoxide, and nitrogen, and an appreciable quantity of dissolved hydrogen. The liquid, which is called the *methane fraction*, is passed into the third heat-exchanger after part of it has been evaporated in precooling the nitrogen.

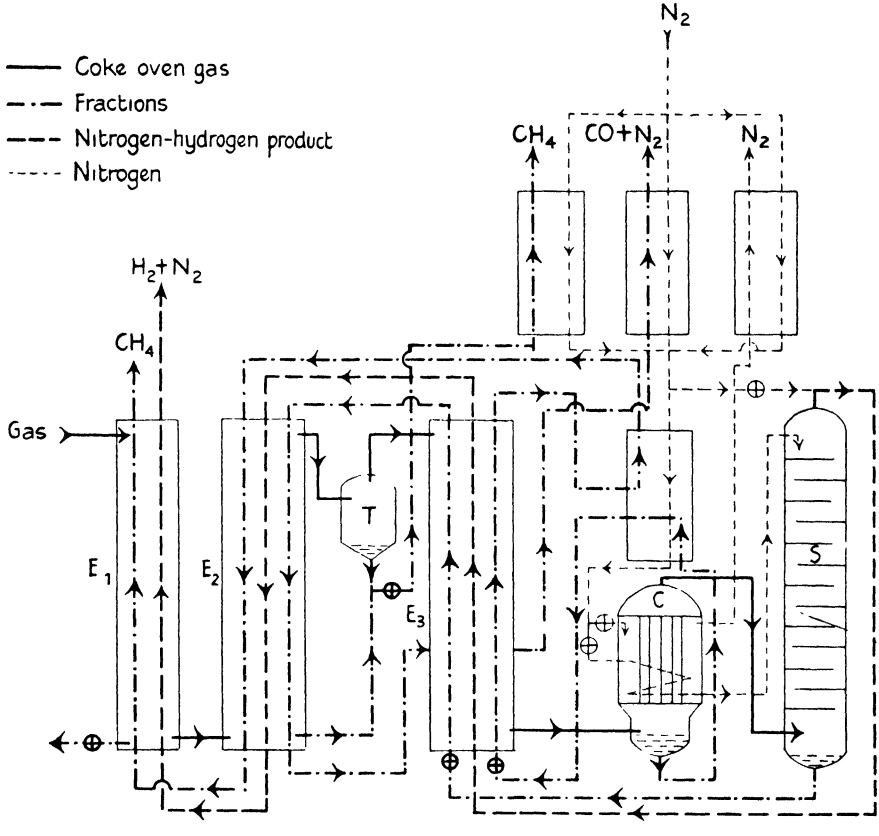


FIG. 142. The Linde-Bronn process for separating coke-oven gas

The portion of the coke-oven gas which remains uncondensed in the liquid nitrogen consists of hydrogen, nitrogen, and carbon monoxide, with only traces of oxygen and methane. It must now be treated in such a way that only hydrogen and nitrogen remain. This is achieved by scrubbing it with liquid nitrogen in a long plate column *S*. The gas enters the column from below and the liquid nitrogen is introduced at the top. A liquid fraction is formed at the base of the column, consisting mainly of carbon monoxide and nitrogen. It also contains all the methane and oxygen residue that was left over from the methane

condenser. The additional nitrogen, required to bring the composition up to the right proportion, is added to the product as it leaves the plate column.

The following tables show the amounts and compositions of the various fractions and gaseous mixtures as obtained in a German plant under typical conditions. The rich gas is obtained by mixing all three fractions and the gas regenerated from the purification plant.

TABLE 25. *Composition of Coke-oven Gas in the Stages of the Linde-Bronn Process*

Crude Gas

	% *by vol.*	*cu. m.*
H_2	46·5	780
CH_4	26·2	440
N_2	13·1	220
CO	6·3	106
CO_2	3·2	54
C_nH_m	2·6	44
C_2H_6	1·0	17
O_2	1·0	17
	99·9	1,678

Purified Gas

	% *by vol.*	*cu. m.*
H_2	49·3	755
CH_4	26·6	407
N_2	13·7	210
CO	6·6	101
CO_2	..	..
C_nH_m	1·8	27
C_2H_6	1·0	15
O_2	1·0	15
	100	1,530

Ethylene Fraction

	% *by vol.*	*cu. m.*
C_2H_4	30·6	15
C_3H_6	6·1	3
C_2H_6	30·6	15
CH_4	30·6	15
CO	2·0	1
	99·9	49

Methane Fraction

	% *by vol.*	*cu. m.*
CH_4	74·4	372
C_2H_4	1·9	9·5
O_2	1·2	6
CO	9·6	48
H_2	4·2	21
N_2	8·7	44
	100	500·5

Carbon Monoxide Fraction

	% *by vol.*	*cu. m.*
CO	18	52
O_2	2	6
CH_4	6·9	20
N_2	73·1	212
	100	290

Rich Gas

	% *by vol.*	*cu. m.*
CH_4	46·5	437
N_2	28·3	265
CO	11·3	106
H_2	4·9	46
C_nH_m	3·9	37
CO_2	1·9	18
C_2H_6	1·4	13
O_2	1·4	13
	99·6	935

Product

	% *by vol.*	*cu. m.*
H_2	75	734
N_2	25	245
	100	979

The final product and the three separate fractions, the latter expanded to atmospheric pressure, pass out of the plant after surrendering their cold to the incoming coke-oven gas and partly to the compressed nitrogen. The final product, the carbon monoxide fraction, and the methane fraction traverse the third and second heat-exchangers, the latter after exchanging some heat with the nitrogen. Only the methane fraction and the product return through the first heat-exchanger. The carbon monoxide and the ethylene fraction are used to precool the nitrogen.

Pure nitrogen, compressed to 180 atm., and taken from an air-separating plant, is precooled in a complicated system of heat-exchangers mainly with the help of the low-pressure nitrogen evaporating in the condenser. But, as mentioned above, the whole ethylene fraction and parts of the other two fractions are also utilized to cool the nitrogen. From different parts of this heat-exchanger system the nitrogen branches off to serve its three purposes. One portion is expanded to atmospheric pressure and, partially liquid, is introduced between the tubes of the condenser. Another part is expanded to 13 atm., completely liquefied in a coil within the condenser, and admitted at the top of the plate column to scrub out the carbon monoxide; a third part is also expanded to 13 atm., and added to the product to bring about the required composition.

The low-temperature part here described is only one part of the aggregate for separating coke-oven gas. Apart from the air-separating plant needed to produce the nitrogen, the aggregate contains an intricate apparatus to purify the coke-oven gas before it is cooled to low temperature, and a large ammonia refrigerator. Crude coke-oven gas contains considerable quantities of benzene, toluene, and xylene, which may or may not be removed in the coking plant before the gas enters the separating unit. If they have not been withdrawn beforehand, the equipment for their removal forms an important unit in the gas-separating plant. In some plants benzene and similar constituents are removed by absorption, but in large-scale aggregates this is impracticable, and it is customary to condense or freeze out the benzene vapour together with some of the moisture. This is achieved in a refrigerating plant using liquid ammonia. But this unit is separated from the actual low-temperature plant described above, except in so far as the same ammonia compressor serves both systems. The coke-oven gas, after passing through the benzene unit, emerges at room-temperature and must then again be cooled to $-45°$ C. with liquid ammonia before it proceeds farther.

In the usual type of plant the benzene unit consists of two pairs of heat-exchangers working alternately. The crude gas is first precooled to about +10° C. in one exchanger by means of cold purified gas and then further cooled to −40° in a second heat-exchanger, supplied with liquid ammonia boiling under reduced pressure. Benzene and similar constituents are thus deposited, mainly in the liquid state, and drained off. At the same time, water is condensed and some ice formed on the surface of the exchanger. The dry gas, freed from benzene, etc., is passed back through the first exchanger, which it leaves close to room-temperature, after precooling the incoming crude gas. After some time the two exchangers become clogged with ice and have to be warmed up. This is done by turning the current of gas into the other two heat-exchangers of the pairs mentioned above. The purified warm coke-oven gas is then passed through one of the cold heat-exchangers, which is thus warmed up again, the ice melting and draining away. At the same time the ammonia heat-exchanger is traversed by warm ammonia. In this way, by reversing the current at intervals, the plant can function for several months without a stoppage.

The Linde-Bronn process has recently been developed to produce technical hydrogen of 97–98 per cent. purity. This entails the removal by partial condensation of almost all the nitrogen in the product leaving the scrubbing tower, and the addition of nitrogen to this product behind the tower is, of course, no longer necessary.

Reference to Fig. 37 on p. 51 shows that it is not possible to obtain sufficiently pure hydrogen as long as the temperature is not lowered below the boiling-point of nitrogen (77·3° K.). The closed equilibrium curve for 78° K. nowhere approaches the hydrogen ordinate closer than to about 93 per cent. H_2. On the other hand, the curve for 63° K. approaches to within 2 per cent. of pure hydrogen at a pressure of about 16 atm. abs. Above this pressure the hydrogen content of the vapour gradually decreases and at lower pressures it falls off rapidly.

Accordingly, for the production of hydrogen, the pressure in the Linde-Bronn plant is raised to 16 atm. abs. and an additional nitrogen condenser is added above the scrubbing column. This condenser is cooled with liquid nitrogen from the nitrogen circuit boiling at a very low pressure and maintained at a temperature of about 63° K. with a two-stage vacuum pump. 63° K. is the triple-point of pure nitrogen and the triple-point pressure is 9 cm. of mercury. Generally, if the nitrogen is not quite pure, the freezing-point is lower than the triple-point of the pure substance, but this is not the case if the impurity is

carbon monoxide, which forms mixed crystals with solid nitrogen. However, the refrigerant nitrogen will contain traces of oxygen, so that it may be possible to cool it slightly below 63° K. with a sufficiently strong vacuum pump without the formation of a solid phase. It may thus be assumed that the condensed nitrogen really is cooled to its triple-point.

Apart from these alterations the Linde-Bronn plant remains virtually unchanged when producing hydrogen instead of a stoichiometric hydrogen–nitrogen mixture for ammonia synthesis.

3. The scrubbing of ternary mixtures

With the help of considerations in this and former chapters, most of the processes occurring in the Linde-Bronn plant can be understood without further explanation, more especially the formation of one liquid fraction after another in the various heat-exchangers and the condenser. It is, however, difficult to calculate accurately the amount and composition of each fraction separately, since this not only depends on the variable composition of the crude gas, but also requires a very accurate knowledge of the equilibrium diagrams of the complicated systems of which the fractions consist. Always at least three and mostly four components are involved in a fraction, and we can form only an approximate picture of the phases formed by neglecting one or other of the components occurring in small concentrations. Our present knowledge of the binary and ternary systems occurring in coke-oven gas is rapidly supplying us with the information necessary. Thus recent investigations on the ethylene–methane system contribute considerably to our understanding of how the ethylene fraction is formed, and the work published on the H_2–CH_4, H_2–N_2, N_2–CH_4, and H_2–N_2–CH_4† systems enables us to work out fairly accurately the composition of the methane fraction as a function of temperature and pressure.

We have, however, come up against one new feature in the Linde-Bronn process which requires some further thought; and that is the scrubbing column, in which carbon monoxide and remnants of other constituents are removed from the final product. This apparatus differs from the plate columns we have discussed in previous chapters in that a special scrubbing liquid, which is not a part of the gas to be separated, is introduced at the top of the tower.

The question arises as to whether the scrubbing process occurring in this unit is essentially the same as or different from what takes place in a rectifying column.

† See Chapter II.

As we have seen, rectification is based on the differences in vapour pressure of two components of a mixture at the same temperature. These differences lead to the particular shape of the equilibrium curves and thence to the fact that a vapour and a liquid in equilibrium with one another have different compositions. Does this hold for a scrubbing process?

We can answer this question and obtain an insight into what happens in a scrubbing column† by considering the equilibrium curves of the ternary system H_2–N_2–CO, which were shown in Fig. 38, p. 52. For our purpose it will be sufficient to take only these three components into account, since the remnants of oxygen and methane have no appreciable part to play in the process. Since their boiling-points are higher than those of the other components, they will naturally collect in the carbon monoxide fraction.

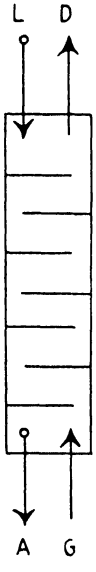


FIG. 143. Schematical scrubbing column

The boiling-points of nitrogen and carbon monoxide are only 6° apart, and throughout the column the concentration of nitrogen is everywhere higher than that of CO. The difference in temperature between the top and bottom of the plate column will therefore be small, probably less than 2° C. Therefore, although the small temperature heads between the plates of the column will play a considerable part in the exchange process, they will have little or no effect on the actual equilibrium curves. In the case of these H_2–N_2–CO mixtures, we are thus fortunate enough to be able to represent the phenomena within the plate column on a single triangular diagram for constant pressure and temperature. This greatly facilitates the theoretical treatment.

Now let us consider a scrubbing column, as shown schematically in Fig. 143. A saturated vapour G, containing hydrogen, nitrogen, and carbon monoxide, enters the bottom of the column, and pure liquid nitrogen L is introduced at the top. A vapour D, consisting almost entirely of hydrogen and nitrogen, leaves at the top, and a liquid carbon monoxide fraction A is withdrawn at the base.

Let x be the CO-concentration of a mixture and m its mass. Since the latent heats of evaporation of nitrogen and carbon monoxide (1,336 and 1,414 cal./mole respectively) are very similar, we can

† See M. Ruhemann and N. Zinn, *Phys. Zeits. d. Sowjetunion*, **12**, 389 (1937).

assume that the amounts of vapour and liquid are the same on each plate.

Then the CO balance equation for the column as a whole reads

$$x_A m_A - x_L m_L = x_G m_G - x_D m_D. \tag{1}$$

But according to our assumptions

$$m_A = m_L, \qquad m_G = m_D, \qquad x_L = 0.$$

Therefore

$$x_A = (x_G - x_D) m_G / m_L, \tag{2}$$

or, if we can assume that $x_D \ll x_G$,

$$x_A = x_G m_G / m_L. \tag{3}$$

That is to say, if we introduce in a given time a known quantity of gas m_G with a known CO-content x_G, and if we specify the degree of purity x_D required and the amount of scrubbing liquid m_L used, the CO-content x_A of the liquid fraction is determined. On the other hand, the liquid fraction A obtained cannot contain more CO than is in equilibrium with the ingoing vapour G. The composition of a liquid in equilibrium with G is given by the liquid end F of the connodal through G in Fig. 144. So if we specify m_G, x_G, x_D, and m_L and compute x_A from (2) or (3), the process will be feasible only if the value of x_A obtained, when plotted on the liquid branch of the equilibrium diagram, comes to lie to the left of point F, the end of the connodal through G. If A lies to the right of F, the specified conditions are incompatible with the functioning of the column. In this case, to obtain the required purity at D, starting with a given quantity of composition x_G, we must use more liquid nitrogen. For by increasing m_L, while x_G and m_G remain constant, we can decrease x_A until A comes to lie to the left of F.

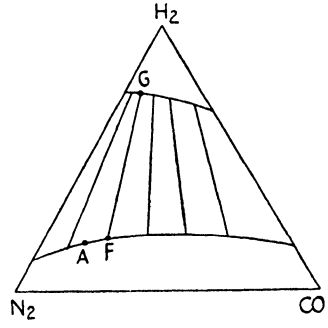


FIG. 144. Schematical equilibrium diagram of CO–N_2–H_2 mixtures, showing what determines the minimum amount of scrubbing liquid

There will thus be a minimum amount of liquid $\bar{m}_L$ which is essential to scrub out carbon monoxide from a given quantity of mixture of known composition, up to a specified degree of purity. This minimum amount of nitrogen will, of course, require an infinite number of plates. In practice, when a finite number of plates of efficiency less than unity is used, m_L will have to be greater than $\bar{m}_L$. Approximate calculations, made with the equilibrium curves of H_2–N_2–CO, showed that, to purify

completely 100 cu. ft. of mixture containing 6 per cent. CO at −190° C., the minimum amount of liquid nitrogen needed varies between values corresponding to 9–12 cu. ft. of gas, according to the pressure used. The most advantageous pressure, from this point of view, is about 20 atm.

Now let us consider the number of plates needed for this process in conjunction with the amount m_L of liquid nitrogen. If we desire a certain degree of purity and fix $m_L > \bar{m}_L$, a definite minimum number of plates is required, which can be ascertained in the following way. Suppose that equilibrium is attained on every plate, and consider an amount of vapour m_G with a CO-concentration x_G, which is to be freed from CO at a definite pressure and temperature. Take a certain value of $m_L > \bar{m}_L$, and a certain very small value of x_D, the CO-content of the final product.

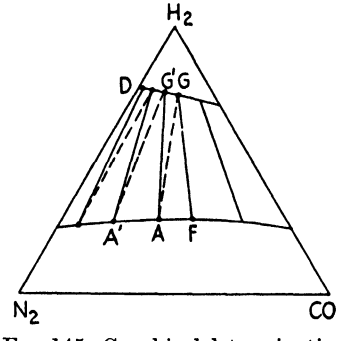


FIG. 145. Graphical determination of the number of plates required in a scrubbing column

Then

$$x_A = (x_G - x_D)m_G/m_L, \qquad (2)$$

and A will lie to the left of the point where the connodal through G cuts the liquid branch of the equilibrium diagram. x_A is then the CO-content of the liquid leaving the lowest plate. According to our assumption, the vapour rising from this plate is in equilibrium with A. It will therefore be represented by the vapour end of the connodal through A (see Fig. 145).

We can determine the composition $x_{A'}$ of the liquid leaving the second plate from below by writing down the balance equation for the whole column, excluding the lowest plate. This gives

$$x_{A'} = (x_{G'} - x_D)m_G/m_L.$$

In this way the composition of liquid and vapour may be found successively for every plate until finally the CO-content has sunk to the value of x_D. The number of steps taken is equal to the minimum number of plates needed.

With this insight into the functioning of the scrubbing column we can find out whether or not scrubbing is identical with rectification. By determining the change in composition from plate to plate we have confirmed the conclusion drawn from the balance equation. Equations (2) or (3) now no longer merely give us the composition of the CO-fraction if it were possible to produce a product free from CO at the

top of the column, but we now know that this product really can be attained.

Now the value of x_A, as obtained from (2) or (3), is quite independent of the shape of the equilibrium curves. It can be changed arbitrarily by varying one of the other independent variables, e.g. m_L, and m_L can always be so chosen as to satisfy the condition that $x_A < x_F$. Indeed, by increasing m_L, x_A can be made as small as we desire. The scrubbing will therefore be effective whatever the equilibrium curves look like, as long as they traverse the whole triangle and there is no critical point at the particular temperature and pressure. Scrubbing does not require a particular relationship between the vapour pressures of nitrogen and carbon monoxide. Indeed, if we call the N_2-content x, instead of the CO-content, we obtain exactly the same equations, and now x_A would have to be greater than x_F. If we wished, we could scrub out nitrogen with carbon monoxide as well as carbon monoxide with nitrogen. This proves that scrubbing is not identical with rectification. We could never reverse the position of oxygen and nitrogen in an air-separating plant.

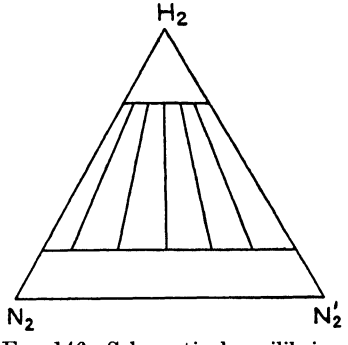


FIG. 146. Schematical equilibrium diagram of mixtures of hydrogen and two forms of nitrogen with identical thermal properties

Yet it would be wrong to say that rectification plays no part at all in the scrubbing process. To understand this, let us consider an imaginary ternary mixture, consisting of hydrogen and two substances with almost identical thermal properties, say two isotopes of nitrogen. The equilibrium diagram of such a system would be of the type shown in Fig. 146. The equilibrium curves would be horizontal straight lines and the connodals would be symmetrical in respect of the altitude of the triangle. We now know that there would be no difficulty in scrubbing out one of the nitrogen isotopes with the other.

Now let us consider the real ternary system. Its equilibrium diagram differs from the imaginary diagram just considered in two respects: the straight equilibrium lines become curves and the connodals are no longer symmetrical. The first is relatively unimportant, but the second is of greater interest. For the difference in the thermal properties of nitrogen and carbon monoxide leads to the fact that there is, as a rule, relatively more CO in the liquid than in the vapour, as compared with nitrogen. The connodals will therefore be turned somewhat in an

anticlockwise direction, as against the symmetrical connodals of the imaginary diagram. A glance at Fig. 145 shows that, for this reason, fewer steps will be required to scrub out CO with N_2 than vice versa, fewer also than to scrub out one nitrogen isotope with another. Fewer plates will therefore be needed. The different thermal properties of nitrogen and carbon monoxide thus facilitate the scrubbing process though they are not essential to it. An approximate numerical calculation shows that these properties cut down the number of plates required by about 30 per cent. This is a measure of the part played by rectification, in the strict sense of the word, in the scrubbing of a ternary mixture.

4. The 'Air Liquide' process

The principal advantage of the Linde-Bronn process for separating coke-oven gas is that it yields a hydrogen–nitrogen mixture that is practically pure. The product frequently contains less than 0·001 per cent. CO and hardly a trace of other impurities. In view of the sensitivity of the catalyst to contamination with CO, this is of particular importance.

On the other hand, the plant described in § 2 is very unwieldy and complicated, especially owing to the large air-separating plant attached to it. This becomes very clear when we consider the course taken by the nitrogen passing through the aggregate. Nitrogen, in the form of atmospheric air, is first compressed and cooled to −190° C. and separated from oxygen in the air column. It is then warmed up again and leaves the air column at room-temperature and atmospheric pressure. Thereupon it is again compressed, this time to 180 atm., again cooled to −190°, and partly liquefied and put to its several uses in the coke-oven gas-separating plant. Again, part of the nitrogen remains pure and can be recompressed and circulated, but a considerable amount is lost in the CO-fraction, where it merely serves to lower the calorific value of the rich gas. All this renders the Linde-Bronn process less economical than could be desired.

Several attempts have been made to replace the Linde-Bronn process by other methods, of which the Claude, or 'Air Liquide', process is the most famous. Claude evidently realized that it would be hardly possible to simplify or increase the efficiency of the Linde-Bronn process without decreasing the purity of the product. On the other hand, it is possible to dispense with high purity if the subsequent ammonia synthesis is carried out at very high pressures. In this case the catalyst is less sensitive to CO and, at very high pressures, the catalyst can be dispensed with altogether. By synthesizing at pressures

of 800–1,000 atm., as against the 300 atm. used in the Haber-Bosch ammonia plant, Claude was able to use a hydrogen–nitrogen mixture containing considerable traces of carbon monoxide. This greatly simplifies the separation of coke-oven gas and enables us to dispense with the scrubbing column altogether.

The elimination of the scrubbing column removes one important source of nitrogen consumption. Another disappears with the necessity of using liquid nitrogen as a refrigerant. According to Claude's well-known principle, all the refrigeration required is taken from the coke-oven gas itself, which is compressed to 25 atm., and then expanded in a cylinder. The high content of hydrogen in coke-oven gas, with its negative Joule-Thomson coefficient, renders the expansion of the gas in a nozzle ineffective from the point of view of refrigeration; on the other hand, it enables lower temperatures to be reached in a cylinder than could be attained with liquid air or nitrogen, especially when, as is the case with this plant, the less volatile constituents are removed before the expansion. Actually the temperatures prevailing behind the expansion engine are frequently as low as −210° C.

In this way the only need for nitrogen is to bring about the stoichiometric composition for the synthesis of ammonia, and this nitrogen can be obtained from a small auxiliary plant.

The compressed coke-oven gas is first passed through a 5 per cent. solution of ammonia, which removes carbon dioxide, sulphuretted hydrogen, and other impurities. The ammonia vapour is then removed with water, and benzene is scrubbed out with mineral oil. The final removal of moisture and CO_2 occurs in a series of drying towers filled with solid caustic soda. Thereupon the gas enters the low-temperature plant.

After traversing one of two alternate heat-exchangers *A* (Fig. 147), in which it is cooled with returning products to −65° C., the gas enters the first separating exchanger *B*, in which a fraction containing mainly ethylene condenses, including some propylene and ethane and a certain amount of methane. If desired, this fraction can be withdrawn in parts, one containing mainly ethylene, another mainly ethane, etc. Thence the gas, after passing through a small additional exchanger *C*, enters the tubes of a condenser *D* at about −100°, in which the methane fraction is liquefied. The liquid fraction is expanded to atmospheric pressure and introduced between the tubes of the condenser. The gas, still containing some methane and most of the carbon monoxide, enters the tubes of a final condenser *E*, in which most of these constituents

are removed. The liquid formed is again expanded and introduced into the condenser, whence it is drained off into *D*, mixing with the methane fraction. The upper part of *E* is separated from the lower by a horizontal partition between the tubes. A mixture, consisting almost entirely of H_2 and N_2, but with rather more CO than in the case of

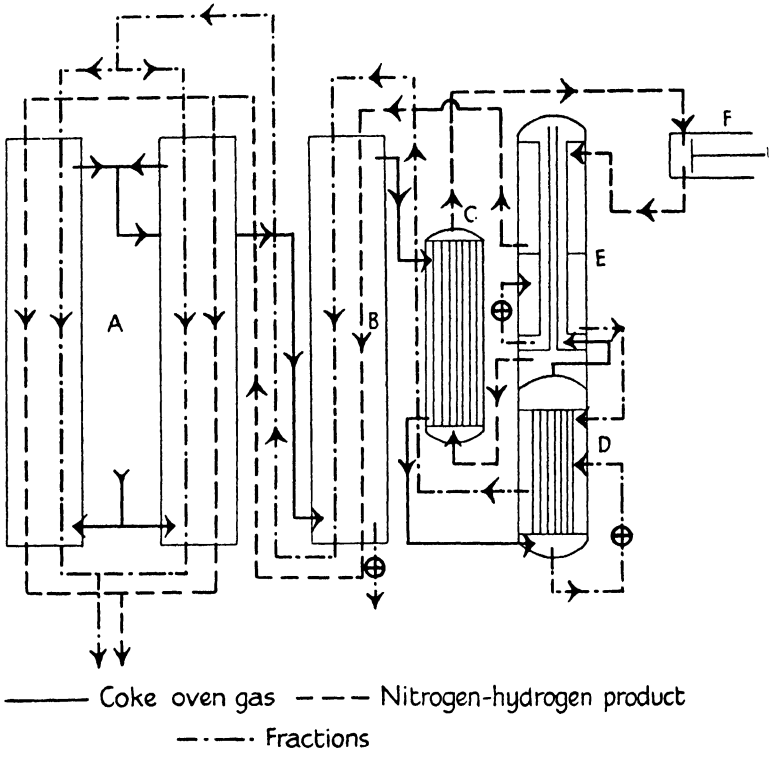


FIG. 147. The 'Air Liquide' process for separating coke-oven gas

the Linde-Bronn apparatus, leaves the bottom of *E*, is slightly warmed in *C*, and enters the expansion engine *F*, where its pressure is reduced to 1 atm., the temperature falling to −200–210° C. This very cold gas forms the refrigerant in the upper part of *E*, which it leaves at about −170°, and passes out of the plant through *B* and *A*. The methane fraction is utilized in the same fashion, precooling the ingoing gas.

The 'Air Liquide' plant exists in several variations, but in all the principal feature remains the expansion engine, which produces all the refrigeration and the very low temperature required to yield fairly pure products without scrubbing. The expansion engine is the only part of the plant erected outside the main lagged casing, and has the

disadvantage of being sensitive and requiring some attention. As in all expansion engines working at low temperatures, the chief problem is lubrication. The lubricant in these engines is liquid nitrogen, which condenses in the cylinder and on the piston during the expansion stroke. Usually there is sufficient nitrogen to cover the requirements, though a considerable quantity is lost in the methane fraction. Occasionally some nitrogen has to be added to improve the lubrication. The expansion engine is often coupled with a small electric generator and some use is made of the power gained. In very large plants it is coupled directly with the compressor. Never more than 30 per cent. of the work done in compressing a gas is regained in an expansion engine. In the case of coke-oven gas, when only about half the gas compressed actually passes through the expansion cylinder, the energy regained is much smaller.

XI

HYDROCARBON GASES

1. Products and raw materials

THE separation of coke-oven gas, as treated in the preceding chapter, was limited to the production of hydrogen, either alone or in conjunction with nitrogen for the synthesis of ammonia. In the plants described the other constituents of the mixture were not separated; on the contrary, the fractions produced in the course of the process were re-mixed and withdrawn together as 'rich gas'. This gas is called 'rich' because of its high calorific value, which is due to the presence in it of a high proportion of hydrocarbons. In the example given on p. 246 the rich gas contained 46·5 mole per cent. methane, 3·9 per cent. of olefines, and 1·4 per cent. of ethane. As was mentioned in Chapter I, these constituents are important, not merely because of their high calorific value, but also as raw materials for chemical industry, which is vitally interested in a supply of pure hydrocarbons, especially olefines. Those which are gaseous under normal conditions of pressure and temperature are of particular importance for several reasons. They are the lightest and simplest compounds, and can therefore most easily serve as elementary 'bricks' for the synthesis of more complex substances, and their isolation in a pure state is on the whole easier than in the case of the heavier hydrocarbons. The more carbon atoms a molecule contains, the greater the number of isomers and compounds of similar boiling-points that are likely to occur with it. The boiling-points of only two hydrocarbons (methane and ethylene) lie between -200 and $-100°$ C., nine boil between -100 and 0° C., and over 30 between 0 and $+100°$ C.

The industrialist can consider the problem of producing pure hydrocarbons from two angles. He can ask himself what products he can obtain from a given raw material, or he can set out to make certain products and decide what are the most suitable raw materials for this purpose. In the same way the scientist can tackle the problem from either side; in fact he cannot avoid doing this if he is to obtain a comprehensive view of the problem as a whole. In Chapter I the various gaseous mixtures were considered, and their approximate compositions listed. In this chapter we shall start with the individual pure substances and find out how they can be isolated from their possible sources.

The choice of a raw material for the production of a given pure hydrocarbon will depend first of all on the availability of the gaseous mixture

TABLE 26. *Hydrocarbon Gases (boiling below 10° C.)*

Name	*Formula*	*Boiling-point °C.*
Methane	CH_4	−161·4
Ethylene	C_2H_4	−103·9
Ethane	C_2H_6	− 88·3
Acetylene	C_2H_2	− 83·6
Propylene	C_3H_6	− 47·0
Propane	C_3H_8	− 42·5
i-Butane C_4H_{10}	$(CH_3)_2CHCH_3$	− 11·7
i-Butylene C_4H_8	$(CH_3)_2CCH_2$	− 6·9
Butylene-1 C_4H_8	$CH_3CH_2CHCH_2$	− 6·3
1, 3-Butadiene C_4H_6	$CH_2CHCHCH_2$	− 4·4
n-Butane C_4H_{10}	$CH_3CH_2CH_2CH_3$	− 0·5
Butylene-2tr. C_4H_8	$CH_3CHCHCH_3$	+ 0·9
Butylene-2cis C_4H_8	$CH_3CHCHCH_3$	+ 3·7
Neopentane C_5H_{12}	$(CH_3)_2C(CH_3)_2$	+ 9·5

sufficiently close to the site of the proposed plant. Gases cannot easily be transported over long distances and it is even more difficult to carry them overseas. Moreover, the crude mixture must be reasonably cheap if the cost of the product is not to be excessive. In general the separation of a pure gas from a mixture will be the cheaper the higher its initial concentration. This is true, not merely for thermodynamic reasons, but also because the capital cost of a plant for separating out a component in low concentration is generally high in relation to the amount of product obtainable. However, this argument need not hold when the crude gas contains other valuable constituents in higher concentrations, so that the major portion of the costs can be borne by these. The choice of a suitable crude gas as a raw material for pure hydrocarbons is thus a complicated matter and requires very careful calculations.

Ethylene

The principal source of ethylene is the gas obtained from oil cracking. As is apparent from Table 7 in Chapter I, this gas can contain as much as 30 per cent. of ethylene and generally contains at least 15 per cent. In oil-bearing countries there is little point in attempting to produce ethylene from any raw material other than cracker gas. The production of C_2H_4 from this source will be described in some detail in the next chapter.

However, large quantities of oil are found in comparatively few countries, and a high proportion of this oil is refined at source. Moreover, not all oil refineries possess cracking units and, with the concentration of the oil industry in the U.S.A., the amount of cracker gas available in Europe is still comparatively small. With the exception of a plant

at Baku, there are no large units in Europe producing ethylene from this gas. Until very recently, it was not the policy of the oil companies to refine in the United Kingdom, and consequently there was no possibility of producing ethylene from oil. The position is now changing and two cracking plants are now being erected, one by Petrocarbon Ltd., and the other by the I.C.I., with the intention of producing considerable quantities of ethylene and other light olefines. It should be noted that these plants are not intended to produce oil fuels at all, but that all the products are to be used in the chemical industries.

For countries not possessing oil resources or refining capacity an alternative source of ethylene is coke-oven gas. This gas, as may be seen from Table 3, Chapter I, generally contains about 3 per cent. of olefines, of which rather more than 2 per cent. usually consists of ethylene.

The production of pure ethylene from a gas in which it has an initial concentration of only 2 per cent. is clearly a difficult and expensive project and it would appear natural to combine this with the production of hydrogen as described in the last chapter. If, for instance, in the Linde-Bronn process, the ethylene fraction were not mixed with the other two fractions, but kept separate and fractionated, it would be possible to produce ethylene in such a way that the major costs of the process could be distributed over the large yield of hydrogen and would not all fall on the small yield of ethylene. As the gas contains about 50 per cent. hydrogen and 2 per cent. ethylene, the ethylene so produced should be very much cheaper than if it were the sole product of the process.

This path was, in fact, followed by the Russian and German industries and in Germany, during the war, considerable amounts of ethylene were made from coke-oven gas, as a by-product from hydrogen plant. Some details will be given in the following section.

There are, however, certain objections to this procedure, only some of which are of a technical nature. The ethylene fraction of a Linde-Bronn plant contains, besides ethylene, ethane and methane in roughly equal quantities, as well as smaller amounts of propylene and carbon monoxide. The ethylene is thus accompanied by constituents with higher and lower boiling-points than itself and its isolation in a pure state therefore requires at least two fractionating columns. Moreover, only 60 per cent. of the ethylene in the coke-oven gas is contained in the ethylene fraction of the Linde-Bronn process. The remaining 40 per cent. is in the methane fraction. To obtain a high ethylene yield, it is

therefore necessary to treat both fractions for ethylene or so to alter the whole process that all the ethylene collects in a single fraction. The Linde-Bronn process itself, as was made clear in Chapter X, is hardly a fractionating process at all. Apart from the scrubbing tower, it relies on partial condensation and this tower itself has neither a re-boiler nor a reflux condenser.

It is therefore clear that the additional equipment required to produce pure ethylene as a by-product of the Linde-Bronn process must be quite considerable and that it will differ markedly from the other units of the plant. If we add to this the consideration that the treatment of the two fractions and the consequent disappearance of the rich gas stream as such will necessarily destroy the balance and hence affect the design of almost every unit, it will be seen that what at first sight might appear to be an insignificant addition, leads in effect to a radical alteration of the entire process.

Besides these technical difficulties there are several economic points that need to be considered. The separation of coke-oven gas for the production of a hydrogen–nitrogen mixture intended for ammonia synthesis leads ultimately to fertilizers, which form a part of the inorganic chemical industry. Ethylene, on the other hand, is primarily a raw material for the organic industry. There are not many industrial firms which combine both these interests and even state-owned industries are generally so departmentalized that a combination of this kind would be inconvenient. But more important than this, the amount of coke-oven gas which would have to be separated in order to produce sufficient ethylene for the needs of the organic chemical industry, would be so great that the amount of hydrogen produced simultaneously would far surpass the demand for synthetic ammonia. Where the hydrogen is to be used for hydrogenation purposes, the first objection would not hold, but the second would still operate. Any such plant would yield about 25 moles of hydrogen for every mole of ethylene, whereas the demand for the two products might be about equal. Clearly if all the ethylene required were produced in this way, there would be no outlet for the hydrogen.

There is a further important economic objection to basing ethylene production on the complete separation of coke-oven gas. This gas is not merely a source of raw materials for the chemical industry, but also an important fuel. A considerable portion of the gas developed during carbonization is used for firing the ovens, some is used as town's gas and some burned for other purposes. There is to-day a shortage of fuel

in Britain as well as in most European countries. If all the coke-oven gas required to cover the needs of the chemical industry for ethylene was completely separated and the hydrogen was also used for chemical purposes, a very large amount of valuable fuel would be withdrawn from the market. This would not be in the interests of the community, even if all the products separated could be usefully absorbed in the chemical industry.

If, therefore, in a country devoid of natural oil resources, coke-oven gas is to be used as a source of ethylene, it is necessary to break the link connecting it with hydrogen and the synthetic ammonia industry and to consider the possibility of separating out ethylene as a primary product while leaving the rest of the gas essentially unaltered. Although, in view of the high calorific value of ethylene, its removal has an appreciable effect on that of the residual gas, it is generally possible in principle to withdraw the whole of the component, together with some of the higher-boiling constituents, such as ethane and propylene, without lowering the calorific value of the gas below 500 b.t.u. per cu. ft. Thus most of the fuel value of the gas is preserved and an important chemical raw material is gained.

The separation of ethylene alone from coke-oven gas involves treating an amount of raw material that is 50 times as great as the amount of final product. Moreover, since the ethylene content is so low, every effort must be made to secure the highest possible yield of the small amount of ethylene present. To obtain ethylene in this way is difficult enough, but to obtain it economically, i.e. at a cost not very much greater than the cost of ethylene from oil gases, is a formidable task. A plant which produces from coke-oven gas pure ethylene and also some pure methane will be described in § 3.

A further source of ethylene was developed in Germany during the war in the form of residual gases left over from the production of acetylene in the electric arc. This process consists essentially in the cracking of methane, and natural gases as well as coke-oven gas were used as a methane supply. Besides acetylene, a certain amount of ethylene is also formed in the arc, and when coke-oven gas is used for acetylene production, the residual gas, after the removal of the acetylene, contains rather more ethylene than the initial gas. When the original raw material is natural gas, the ethylene content of the residual gas is lower, about 1 per cent., and the gas is otherwise very similar to coke-oven gas. This gas was used to produce technical hydrogen (97 per cent.) and a crude ethylene fraction was also obtained which was worked

up to 95 per cent. ethylene. In some cases the residual gas from the arc was mixed with other gases obtained by the hydrogenation of coal or lignite, which have a higher ethylene content and are rather similar to cracker gases.

Methane

A number of actual and potential uses of methane were mentioned in Chapter I in connexion with natural gas, of which it is the main constituent. In most of the countries possessing natural gas wells, some of these consist of almost pure methane, and this gas is available in sufficiently large quantities and at so low a price that it can be used as a fuel or as a chemical raw material without the problem of gas separation arising at all. In these countries the problem is rather to find a suitable use for the available methane, rather than to look for sources to cover existing requirements.

However, even in many countries lacking natural gas resources, there is no apparent shortage of methane. Methane is present as fire-damp in most coal seams, it is an important constituent of town's gas, coke-oven gas, and low-temperature carbonization gas, it appears in all refining and hydrogenation processes, whether based on oil, coal, lignite, or peat, it is an essential by-product of wood distillation and it is evolved during the anaerobic fermentation of sewage. But in all these cases it is more or less diluted with other constituents and can be obtained in a pure state only by some form of gas separation. Table 27 shows the approximate methane content of some of these gases together with the principal constituents present.

TABLE 27. *The Sources of Methane*

Source	*Mol.* % CH_4	*Other constituents*
Natural Gas . .	70–100	C_2H_6, C_3H_8, C_4H_{10}, N_2
Coke-oven Gas . .	20–35	H_2, N_2, CO, C_2H_4
Town's Gas . .	25–40	H_2, N_2, CO, C_2H_4
Cracker Gas . .	30–45	H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8
Sewage Gas . .	65–70	CO_2

At the time of writing very little methane is available in Britain. A number of blow holes exist in Scotland, Wales, and Staffordshire from which gas is emitted containing about 95 per cent. CH_4, but the gas is not available for industrial purposes. Small quantities are obtainable from several modern sewage works, in particular at Isleworth and Birmingham, where facilities exist for compression and purification. The sewage gas containing 70 per cent. CH_4 and 30 per cent. CO_2 is scrubbed

with water at low pressure and compressed into cylinders. The purified gas contains about 97 per cent. CH_4, the rest being CO_2, H_2, and O_2. The latter are introduced from the scrubbing water.

Pure methane is also being produced at the British Oxygen Co.'s plant at Corby, where it appears as a by-product of ethylene.

Some liquid methane is obtainable from the Linde-Bronn plant of Nitrogen Fertilizers Ltd., Flixborough, Lincs., in which there are facilities for purifying the methane fraction. Liquid methane was taken from this source for large-scale tests on its use as a fuel for driving buses.† A further source of liquid methane will shortly be available from the cracking plant now being erected by Petrocarbon Ltd., at Carrington, Cheshire.

There is at present no regular demand for methane in Great Britain, but should it arise, there is no doubt that quite large supplies would be forthcoming from all the sources listed in Table 27. From many angles this would be a desirable development. For one thing it would greatly improve the economics of ethylene production from coke-oven gas. It would be very difficult to carry out such a process economically with ethylene as the only product, but if a certain amount of methane could be disposed of simultaneously at a price somewhat above the normal fuel value, the position would be quite different. A coke-oven gas from which the ethylene had been removed, together with, say, twice the amount of methane, would still have an adequate calorific value for most purposes.

Consider, for instance, a gas containing 50 per cent. H_2, 30 per cent. CH_4, 10 per cent. CO, and 2·5 per cent. olefines, with a gross calorific value of 555 b.t.u./cu. ft. moist. If the ethylene were substantially removed, leaving 0·5 per cent. olefines in the gas (propylene and residual ethylene), the calorific value would be 503. If, in addition, an amount of methane were removed equal to 2·5 times the volume of ethylene product, the calorific value of the residual gas would still be 453. If the plant were designed to produce 5,000 tons of ethylene per annum, it would supply 7,000 tons of methane and leave a valuable gas as residue with 93 per cent. of the volume of the initial gas treated.

The use of methane as a raw material in the chemical industry was discussed in Chapter I and also its potential importance as a high-octane fuel for internal combustion engines. Its position as a constituent of town's gas with a high calorific value has led to a further suggestion for its use in this connexion. Apart from short-term daily peaks, the gas

† A. C. Egerton, F. A. Hall, and M. Pearce, *Journ. Inst. Fuel*, **19**, 193, June 1946.

industry has to allow for long-term seasonal load variations which call for the provision of much stand-by equipment owing to the impossibility of storing large quantities of gas. The average load factor in the gas industry is therefore low and large sums have to be sunk in capital investment. When natural gas is used for domestic and industrial heating, as in America and the U.S.S.R., the gas may be liquefied for storage as previously described. Town's gas cannot be so liquefied in view of its hydrogen content. The temperatures required would be so low as to make the costs of liquefaction prohibitive with the existing technique. It is, however, possible to extract some of the methane from the gas, presumably together with small quantities of olefines and ethane, and to liquefy this for storage. At the same time modern methods of gas making, such as gasification of coal with steam and oxygen, enable a gas to be produced of a composition similar to town's gas, but with a variable methane content. If desired, the methane concentration in this gas can be raised from 25–35 per cent. to 50–60 per cent., with a corresponding increase in the calorific value.

It has been suggested that, during the summer months, when the load factor is low, the gas industry should make gas containing surplus methane, that so much methane should be extracted, liquefied, and stored as will bring the calorific value of the residue down to the standard figure, and that this methane should be re-evaporated in winter, when the load factor is higher. This methane could then be used to raise the calorific value of additional lean gases such as water gas or producer gas, made during the winter period, to the standard figure, or the additional load could be covered by simply raising the calorific value of the gas delivered to the consumers.

No doubt a number of difficulties would have to be overcome before this scheme could be realized, but it offers interesting possibilities in the field of fuel economy and at the same time raises new problems for the separation of gases.

Propylene and Butylenes

The propylene content of coke-oven gas is generally below 1 per cent., and it is unlikely that the increasing demand for this gas by the chemical industry can be met economically from this source. As mentioned previously, no olefines are present in natural gases. The principal source of propylene and of other light olefines is cracker gas from the oil refineries, and its production on a commercial scale has long been established in the U.S.A. and the U.S.S.R. Alternative sources for

countries based on coal are low-temperature carbonization gas, in which the propylene content is two or three times as high as in coke-oven gas, and the gas obtained by coal hydrogenation. Butylenes, especially isobutylene, can be obtained by the dehydrogenation of butane as well as from cracker gas. The C_4 content of gases derived from coal is generally quite small.

Propane and Butane

As may be seen from Table 6 in Chapter I, some natural gases contain quite large proportions of propane and butane, and in oil-bearing countries this is one of the principal sources of light paraffins. The natural gases with high propane and butane contents are those most closely linked to mineral oils and are frequently 'wet' gases from which oil can be recovered. These oils are invariably 'wild', that is to say, they contain too many volatile constituents, and have to be 'stabilized' in fractionating columns. Here the lightest constituents, in the main propane and butane, are stripped off. The mixture may be used directly as fuel, or separated by further fractionation if required. Many natural crude oils are also 'wild' and require similar treatment.

The stabilizer is the point where oil refining and gas separation meet, as it deals with substances which are partially gaseous and partially liquid under normal conditions of temperature and pressure. Stabilizers generally work at elevated pressures so that refrigeration is not required, and they are built according to designs characteristic of the oil industry. They are typical units for the treatment of multi-component mixtures which the oil industry had developed to high perfection in the last decade.

Propane and butane may also be obtained from low-temperature carbonization gases and from most hydrogenation processes.

Ethane

This gas is not yet in great demand for the chemical industry and is generally used as fuel. It is contained in all gases from which ethylene may be removed and in most natural gases. It is generally left in the gas after other constituents have been withdrawn in view of its high calorific value.

2. The production of ethylene from the Linde-Bronn fraction

As was discussed in the previous section, ethylene may be obtained from coke-oven gas either in conjunction with hydrogen or hydrogen–nitrogen mixtures in the course of the complete separation of the initial

gas, or the coke-oven gas may be left substantially unchanged and the ethylene removed alone, with or without a certain amount of methane.

The German Linde Co. produced ethylene during the war in conjunction with technical hydrogen from Linde-Bronn plants, modified as described on p. 248. The process was linked with the production of acetylene in the electric arc, for which the raw material was either coke-oven gas or natural gas or a mixture of the two. The composition of the gas after leaving the arc and after scrubbing out the acetylene and the CO_2 is fairly similar whatever its origin, as the process in the arc cracks the hydrocarbons, producing large amounts of hydrogen. If natural gas is used, the ethylene and CO contents are lower, as is evident from the following typical analysis:

TABLE 28. *Analysis of Residual Gas from Arc*

	Gas from arc using natural gas	*Typical coke-oven gas*
C_nH_m	0·9	3·3
CO	2·0	8
H_2	55·2	49·5
CH_4	33·5	29
N_2	8·0	10
O_2	0·4	0·2

When coke-oven gas was used in the arc, the residual gas passed to the Linde-Bronn plants contained slightly more ethylene than the coke-oven gas itself.

In this process the ethylene fraction from the Linde-Bronn plant is worked up to 95 per cent. ethylene in a separate plant after warming up and recompressing. The coke-oven gas-separating plant itself differs from those previously described only in that the ethylene fraction is kept separate from the remaining rich gas.

As in the normal Linde-Bronn plants (see p. 244) the C–3 hydrocarbons and most of the ethane condensed between the first two exchangers and the ethylene fraction is liquefied in the second exchanger and collects in the ethylene trap. But as the pressure is now 16 instead of 13 atm. so as to enable 97 per cent. hydrogen to be produced (see p. 248), almost all the ethylene appears in this fraction and very little is carried over into the methane fraction. At the same time, more methane is liquefied with the ethylene, so that the ethylene fraction contains only 19 per cent. C_2H_4 when working on coke-oven gas, as against some 30 per cent. C_2H_4 in the normal Linde-Bronn plant. When

the process is based on natural gas, the ethylene fraction contains only 6 per cent. C_2H_4. In this case the fraction was sometimes mixed with an ethylene fraction from a hydrogenation plant, giving an ethylene content for the final crude fraction of 25 per cent. C_2H_4.

The composition of the various streams of the Linde-Bronn plant when the process is based on natural gas is as follows (the plant deals with 9,200 m.³ of gas per hour):

TABLE 29. *Composition of Streams in Linde-Bronn Plant producing Hydrogen and Crude Ethylene from Natural Gas after Acetylene Production in Arc*

	Gas from arc		*Crude* C_2H_4	CO *fraction*	CH_4 *fraction*	H_2 *product*
	m.³	*Mol* %	*Mol* %	*Mol* %	*Mol* %	*Mol* %
CO_2	1	0·01	0·1	0	0	0
C_2H_2	9	0·1	0·2	0	0	0
C_nH_m	83	0·9	6·0	0	0·6	0
CO	184	2·0	1·5	13·5	4·0	0
H_2	5,063	55·0	2·5	5·5	5·2	97·0
CH_4†	3,080	33·5	82·0	8·7	80·0	0
N_2	735	8·0	9·0	71·5	10·0	2·9
O_2	37	0·4	0·3	0·5	0·3	0·1
	9,192 m.³		1,080 m.³	450 m.³	2,660 m.³	5,000 m.³

† contains some C_2H_6.

When the raw material is coke-oven gas the olefine content of the crude ethylene is higher and the methane content lower.

The crude ethylene leaves the Linde-Bronn plant warm and is compressed to 3 atm. and precooled to −55° C. in counter-current with its products. The production of 95 per cent. ethylene from this mixture is carried out in two fractionating columns, known respectively as the methane and the ethylene column. The procedure, which is a very typical solution for this kind of problem, is shown schematically in Fig. 148.

The crude ethylene fraction is partially liquefied in a re-boiler situated in the sump of the methane column (1). It is further cooled in counter-current with gaseous methane and expanded to 2 atm. abs. whereby a part of the condensed methane flashes and leaves the plant together with all the nitrogen and carbon monoxide. The remaining liquid, containing practically all the olefines and part of the methane, is then introduced at the top of the methane column. This column removes the methane and lower-boiling constituents from the ethylene and higher-boiling components. The former leave the column as 'overhead'

together with the flash-gas and are warmed up in the exchanger, finally rejoining the rich gas from the Linde-Bronn plant. The latter are introduced as a liquid into an intermediate plate of the ethylene column (2) after expansion from 2 to 1·6 atm. abs. This column separates the ethylene from the higher-boiling constituents ethane and propylene. The reflux liquid and the heat for the re-boiler are supplied by a separate ethylene cycle working between 7 and 1·6 atm. abs. This ethylene,

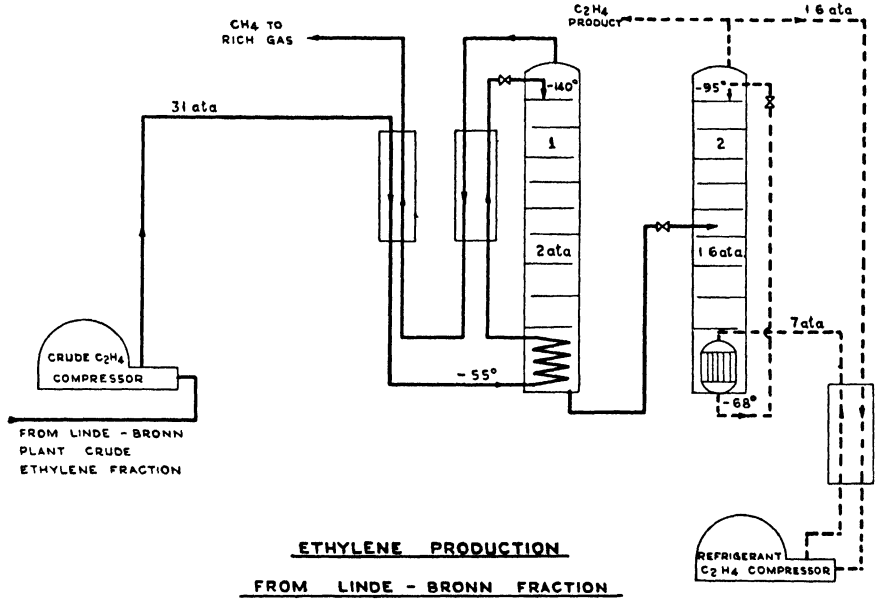


FIG. 148

compressed to 7 atm., is liquefied, after precooling with low-pressure ethylene gas, in the re-boiler of the column and is then injected at 1·6 atm. at the top of the column. Of the gaseous ethylene leaving column (2) as overhead a part is removed as product, while the rest is returned to the ethylene compressor thus forming a refrigerating cycle. The amount of circulating ethylene remains the same throughout and is governed by the reflux ratio required in the column; the product contains the ethylene introduced with the crude ethylene fraction.

This plant contains a number of important features which have become typical for the separation of hydrocarbon gases and which merit more detailed consideration.

It will be noted that neither of the two columns features a reflux condenser, but that the method of supplying reflux is different in the

two cases. The reflux for the methane column is the liquid mixture itself, which is introduced at the top of the tower, while the reflux for the ethylene column is injected from a separate ethylene cycle.

From our discussion of the separation of air (see p. 141) it is apparent that the methane column corresponds to a single-column air-separating plant, and it was shown in Chapter VI that such a plant could produce pure oxygen but not pure nitrogen. The gas leaving the top of the column could not contain a higher percentage of nitrogen than was in equilibrium with the liquid air entering the column.

We should therefore expect the same conditions to hold in the methane column of the plant now under consideration. Taking the feed to consist substantially of methane and ethylene, while neglecting the other constituents as a first approximation, the gas leaving the top of the column cannot contain a higher percentage of methane, or a lower percentage of ethylene, than corresponds to a vapour in equilibrium with the liquid entering the column. It would therefore seem that the methane leaving as overhead must be severely contaminated with ethylene and that this must seriously lower the ultimate ethylene yield from column (2).

However, the situation is not quite as serious as might appear, since the equilibrium curves of methane–ethylene mixtures are rather different from those of mixtures of oxygen and nitrogen. Since the normal boiling-points of ethylene and methane are 58° apart, as compared with 13° in the case of oxygen and nitrogen, the inhomogeneous regions on the (T, x) diagrams are much wider and the ethylene content of vapours in equilibrium with liquids containing a high percentage of ethylene are quite small. Whereas the vapour in equilibrium with liquid air (21 per cent. O_2) at atmospheric pressure contains 7·5 per cent. O_2, the ethylene content of vapours in equilibrium with methane–ethylene mixtures at 2 atm. abs. is as follows:

Temperature °C.	*Ethylene in liquid* *Mol* %	*Ethylene in vapour* *Mol* %
−130	75·0	6·5
−135	66·9	4·2
−140	51·5	2·0
−145	37·8	0·4

These figures show that, as long as the ethylene content of the liquid entering at the top of the column is not higher than about 50 per cent., the amount of ethylene lost with the overhead vapour need not be excessive. In the crude ethylene fraction described in Table 29, the

methane–ethylene ratio is over 13:1; in coke-oven gas fractions it is about 4:1, and in the strongest ethylene mixtures obtained by adding hydrogenation gas to the crude fractions the ratio is about 2·5:1. Hence it is only necessary to cool the fraction far enough to prevent more than 50 per cent. flashing on expansion to 2 atm. in order to keep the ethylene losses to a very low figure. In fact, the top of the methane column has a temperature slightly below −140° C. and the single column is quite adequate to ensure a high ethylene yield.

The great advantage of this arrangement is that it renders unnecessary the provision of a further low-temperature refrigerating cycle, like the ethylene cycle which operates the column (2). Such a cycle would have to use pure methane as the working substance and would have to work between 2 and about 36 atm. It would greatly add to the cost of the equipment and would probably use more power than is needed with the existing arrangement.

Turning now to the ethylene column and the ethylene refrigerating cycle, it is seen that the ethylene is liquefied in the sump of column (2), thus operating the re-boiler, and is then expanded and injected at the top of the column providing reflux at a lower temperature. It is inherent in the principle of a rectifying column that the top is at a lower temperature than the bottom, and in every column containing a rectifying and a stripping section, heat must be introduced at the bottom and withdrawn at the top. It is therefore reasonable to seek to combine these two operations with a single refrigerating machine, using the sump of the column as a condenser and a reflux condenser as the evaporator. This is the principle of the heat pump, whose coefficient of performance is the higher, the smaller the temperature difference between condenser and evaporator. It is therefore almost always economical to use a heat-pump cycle for a rectifying column when the required reflux ratio is fairly high and the temperature difference between the top and bottom of the column is fairly small.

In the ethylene column now under consideration, the heat pump operates between −90° and −68° C. and between 2 and 7 atm. abs. The reflux ratio is 3:1, and these conditions are quite favourable. The temperature difference would be still smaller and the reflux ratio higher if the column dealt with ethylene and ethane only. The presence of propylene in the mixtures simplifies the operation of the column.

A further important principle is illustrated in this column in the direct injection of the ethylene refrigerant. According to classical distillation practice, a column should have a re-boiler and a reflux

condenser. In this column there is no reflux condenser and the reflux ethylene is introduced directly into the column from the heat-pump cycle. This arrangement is possible when the refrigerant and the overhead product are the same. Its advantages are that it saves the considerable expense of a reflux condenser, which in large columns with high reflux ratios may involve many thousands of tubes, and that no temperature difference is required between the refrigerant and the product. In view of the low thermal conductivity of hydrocarbons, it is difficult to bring about a high heat transfer coefficient between the two sides of a reflux condenser. Therefore, if the heat-transferring surface is to be reasonably small, a temperature difference of about 4° will subsist across it. This means that the temperature of the refrigerant must be 4° lower than that required for the product, and at low temperatures every degree costs more power and 4° may be important. The disadvantage of direct injection of refrigerant is that it links the refrigerant cycle very closely with the main stream and any accident occurring in the latter immediately affects the former. This makes direct injection difficult when the plant has to run under variable conditions. Suppose, for instance, in the plant now under discussion, the composition of the crude ethylene fraction varies, perhaps by the introduction of more rich fraction from a hydrogenation plant. This will alter the conditions in column (1) and the composition of the feed to column (2). This again will call for a change in the reflux ratio of column (2) and it may be necessary to speed up the heat pump. If the adjustment is not carried out correctly, some ethane and propylene may penetrate into the overhead of column (2). If the latter is equipped with a reflux condenser, this has no effect on the refrigerating cycle as such, which can then be adjusted at leisure; but with direct injection the fouled product is drawn into the refrigerating cycle itself and steps have to be taken to restore the composition. This may make the regulation of the plant difficult.

3. The production of ethylene from coke-oven gas without complete separation

The British Oxygen Co. have recently erected a plant at Corby, Northants, in which pure ethylene and some methane are recovered from coke-oven gas without the simultaneous production of hydrogen or a hydrogen–nitrogen mixture.† This plant is of fundamental importance as it will decide the economics of ethylene production from coal.

† P. M. Schuftan, *Chemistry and Industry*, 1948, p. 99; British Patent 526,652.

It is also of great scientific and technical interest since it involves certain new principles in the methods of gas separation.

Attention has already been drawn to the difficulty of recovering ethylene economically from a gas in which it is present at a concentration of only 2 per cent. It is, for instance, almost essential for such a process to be carried out at low pressure, as the cost of compressing to a high pressure an amount of gas fifty times as great as the final product may well be prohibitive in a country like Britain where power costs are high.

In a plant of this kind, where very large quantities of gas are treated at low temperatures for a relatively small amount of product, the power consumption, which is in the main proportional to the refrigeration requirements, is primarily due to incomplete recuperation of cold. The actual amount of cold required to condense out the product is not very great, but any difference in temperature between incoming and outgoing streams appears as a formidable heat leak and requires a great deal of power to produce the compensating refrigeration.

To obtain a picture of the order of magnitude of this effect, consider 5,000 m.^{3} of gas consisting, say, of 98 per cent. H_2 and 2 per cent. C_2H_4. The actual condensation of the 100 m.^{3} of ethylene contained in this gas requires about 12,800 kcal. A large proportion of this will ultimately be recovered since the C_2H_4 is evaporated in the plant. If the crude gas enters the plant at 15° C. and the products leave at 10° C., an amount of cold equal to 6,900 kcal. is irrecoverably lost, and this loss has to be made up by refrigeration at low temperatures, probably at the temperature at which the ethylene is condensed. This shows the importance of good recuperation of cold and leads to the conclusion that this type of plant must have very efficient heat-exchangers so that the temperature difference at the warm end will be a minimum. It was shown in Chapter III that a way to achieve this recuperation is by the use of regenerators.

There are, however, other reasons which call for the use of regenerators in this case. The coke-oven gas is not only moist, but it contains about 2 per cent. of CO_2, that is to say over 60 times as much as the CO_2 content of air and about the same quantity as the desired ethylene product. The removal of this CO_2 by chemical means would be difficult and expensive. Regenerators are the natural way out of the difficulty. They should enable the ice and CO_2 to be deposited in one period and sublimed in the other.

There is still one formidable difficulty to be overcome which is due to the complex nature of coke-oven gas. The gas contains ethane and

propylene as well as ethylene and CO_2. It also carries small amounts of acetylene, nitrogen dioxide, sulphuretted hydrogen, and other impurities. The boiling-points of most of these components lie not very far apart; chemical purification is too dear. The regenerators will have to deal with this also. Table 30 lists some of the components of coke-oven gas with boiling-points higher than that of ethylene, and it must be remembered that, the lower their concentration in the mixture, the lower the temperature at which they will tend to condense.

TABLE 30

Substance	*Boiling-point* °C.
Ethylene	−104
Ethane	− 88
Acetylene	− 82
Carbon dioxide†	− 78
Hydrogen sulphide	− 60
Propylene	− 47
Propane	− 42

† Point of sublimation at 1 atm. abs.

It would, of course, be desirable to deposit all these substances on the regenerator surface with the exception of the ethylene, but this is not possible. If the temperature at the cold end of the regenerator is too low, some of the ethylene will be condensed and thus lost. If the temperature is too high, some of the other substances will pass the regenerator. The best that can be achieved is to deposit the bulk of the higher-boiling components in the regenerator and simultaneously to arrange for most of the ethylene to pass through. A compromise has to be found and the Corby plant actually recovers about 80 per cent. of the ethylene in the gas, most of the remaining 20 per cent. being lost in the regenerators and thus finally returned with the lean gas.

It must be pointed out that the use of regenerators in this plant involves much more than merely adapting a piece of equipment well established in the oxygen industry for the separation of a different gas. In conventional Linde–Fränkl plants the duty of the regenerator, apart from its service as a heat-exchanger, is to prevent ice and small quantities of carbon dioxide from entering and blocking the separating units. The amount of CO_2 retained is negligibly small compared with the amount of product. The Corby regenerators, on the other hand, while performing a similar duty as heat-exchangers and dryers, not only have to deal with far greater quantities of CO_2, but they also play an

important part in the separating process itself. In condensing and re-evaporating the higher hydrocarbons while transmitting the bulk of the ethylene, they are actually replacing distillation equipment, and a detailed analysis of the changes taking place on these surfaces during the two half-periods of the cycle shows a marked fractionation effect which contributes considerably to the separation of the ethylene from the higher hydrocarbons. In this sense the function of the regenerators in this plant represents a fundamental innovation which may, if successful, have an important influence on future developments.

In yet another aspect the Corby regenerators differ from those used in air separation. In the latter the incoming air is at a pressure of 5·5 atm., and the returning nitrogen and oxygen are only slightly above atmospheric pressure. In the Corby plant the coke-oven gas enters at 2·15 atm. and leaves at about 1 atm. abs. In one case the pressure difference between the two streams is over 5 atm., in the other it is just over 1 atm. It was pointed out in Chapter III that the returning gas must be at a lower pressure than the incoming gas in order to ensure the re-evaporation of the deposited substances, especially as the former is at a lower temperature than the latter. It is evident that a given weight of gas can hold a greater quantity of CO_2 and water vapour under equilibrium conditions the lower its pressure. In Linde–Fränkl plants, with the temperature difference usually obtaining at the cold end of the regenerators between the air leaving in one half-period and the products entering during the other half, a pressure difference of about 5 atm. is reckoned to be just adequate to guarantee complete sublimation of the deposited impurities. In the Corby plant a much smaller difference is provided and the regenerators appear to be purged adequately. This difference is probably due in part to the high thermal conductivity and low viscosity of hydrogen as compared with air, which leads to higher mass and heat transfer coefficients and thus requires smaller driving forces.

A schematic flow-sheet of the Corby plant is shown in Fig. 149.

A turbo-compressor (1) brings the main coke-oven gas stream to 17 lb./sq. in. gauge and passes it to the regenerator (2) in which the gas is cooled to −143° C., depositing ice, carbon dioxide, and other impurities, as well as all the propylene, some ethane, and about 15 per cent. of the ethylene. After traversing an equalizing device to reduce the temperature oscillations caused by the switching over of the regenerator streams, the gas passes a series of three partial condensers (3) in which it is split into three fractions. One of these containing practically all the

ethane and ethylene together with some methane, passes as a liquid to the methane column (8). A second liquid fraction consisting almost entirely of methane, serves as reflux in this column. The third portion is the uncondensed gas, containing hydrogen, nitrogen, carbon monoxide and a certain amount of methane. This revert gas, after being heated in the exchanger (4), is expanded in the turbine (5) and returns at low pressure through the regenerator (6). A return-gas booster (7), which

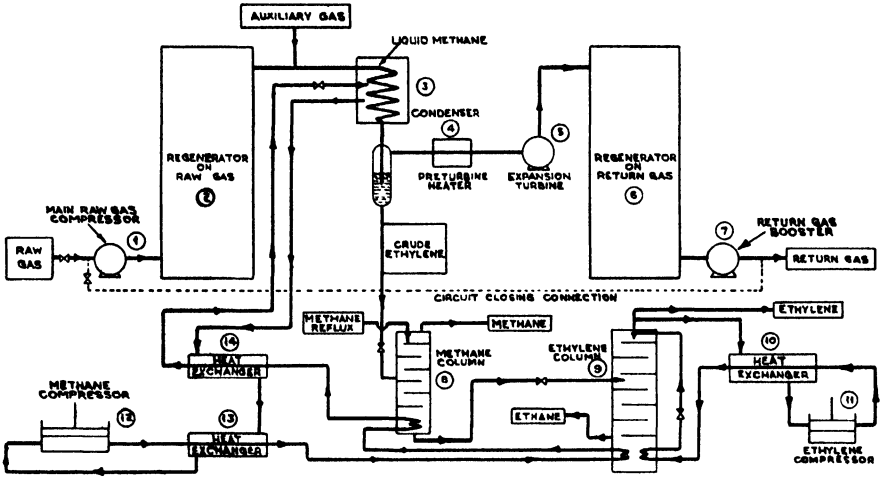


FIG. 149. Plant for producing ethylene and methane from coke-oven gas

takes its power from the expansion turbine, blows it back to the coke-ovens.

In the methane column, which receives its reflux from the methane fraction, the ethylene fraction is stripped of methane, and the liquid bottoms of this column are separated in the ethylene column (9) into pure ethylene and almost pure ethane.

The reflux for this ethylene column is provided by an ethylene heat pump working between 5 and 1 atm. abs., the ethylene being condensed at 5 atm. in the re-boiler and injected at atmospheric pressure into the top of the tower.

One of the three partial condensers (3) which serve to liquefy the fractions is cooled with evaporating liquid methane from a separate refrigerating cycle backed by a small ammonia machine (not shown in the figure). The methane is compressed to 60 atm., precooled with ammonia, and liquefied in the re-boiler of the methane column. A part is injected after expansion into the top of the methane column.

Mainly to balance the regenerators, and incidentally fulfilling some

other useful purposes, a small portion of coke-oven gas, about 5 per cent. of the total quantity treated, is chemically purified, cooled with the returning ethane and ethylene fractions and introduced into the main stream in front of the condensers (3). In this way the products of the process are replaced by an equivalent amount of stripped gas, which equalizes the two streams passing through the regenerators and enables very small temperature differences to be maintained at both ends.

The economics of this plant are determined primarily by the power consumption, and this is strongly dependent on the yield of ethylene, which is about 80 per cent. By the use of the expansion turbine, which works between the narrow limits of 12 and 3 lb./sq. in. gauge, and with the aid of the small subsidiary refrigerating cycles, it is possible to make do with 17 lb./sq. in. gauge at the delivery of the main coke-oven gas compressor and thus to reduce the total power consumption to 3,700 kWh per long ton of ethylene. The plant treats 10,000 m.^{3} of coke-oven gas per hour and is to produce annually 2,000 tons of ethylene.

4. The production of helium from natural gases

As may be seen from Table 6 in Chapter I, some natural gases contain appreciable traces of helium. As these gases consist mainly of methane, and as they form the only economic source of helium, it is natural to consider helium in association with hydrocarbon gases.

Formerly helium was used in large quantities for filling airships. At the beginning of the First World War it was thought that the airship would play an important part in hostilities, and great initiative was shown in exploiting the American and Canadian helium resources. To-day the airship as a military weapon is extinct, and helium is used for filling diving bells and preserving foodstuffs.

It has been found that the richest helium sources are not the gases closely associated with oil but, on the contrary, those rather more remote from the oil fields, which contain a relatively high percentage of nitrogen. It is sometimes said that, the greater the nitrogen content, the greater the probability of finding a high percentage of helium. This is perhaps not strictly true, but it is a fact that where there is no nitrogen there is hardly ever helium. The figures of Table 6 give some impression of the connexion that appears to exist between helium and nitrogen; but it should be pointed out that these figures are somewhat arbitrary samples of a large number of tests and may therefore not be taken as a fair average.

The prevalence of nitrogen in helium-bearing natural gas is of

considerable importance for the technique of helium production. For with a ternary mixture, consisting of methane, nitrogen, and helium, any separating process based on partial liquefaction will lead to methane liquefying first. Since the solubility of helium in liquid methane is very small, the liquid first formed may contain some nitrogen, but all the helium will remain in the gas. Methane and nitrogen are fairly easy to separate, and so the final stage of the process, and the only stage that offers any serious difficulties, will always consist in separating nitrogen and helium. This will hold quite irrespective of whether the original mixture contained 10 or 60 per cent. N_2. Thus, for the production of helium from natural gas, the methane is relatively unimportant, even though it may comprise up to 90 per cent. of the source. It may be of value as a refrigerant, but in the actual separating process we always have to deal with an essentially binary mixture, consisting of helium and nitrogen.

Let us consider such a binary system. The boiling-points of its components lie very far apart. The vapour-liquid equilibrium curves are known (see Figs. 52 and 53). We have already discussed the system in an example in Chapter III and there would appear to be no difficulty in effecting a complete separation by the method of partial liquefaction.

And yet the operation is not quite so straightforward as we might imagine. One difficulty becomes apparent as soon as we consider the purity of the helium to be produced. If this is to be 99 per cent., as is usually required, a considerable strain is put upon the efficiency of the separating plant. The normal boiling-point of nitrogen is 77·3° K., and liquid nitrogen is the coldest refrigerant naturally available. With a refrigerant boiling at 77°, the temperature of the mixture cooled cannot easily be maintained below 80° K. But to remove almost all the nitrogen from a helium–nitrogen mixture at 80° K., fairly high pressures are required. The following are the helium concentrations of vapours in equilibrium with liquids at 80 and 70° K. at various pressures.

TABLE 31. *Helium–Nitrogen Mixtures*

	% He *in vapour at equilibrium*	
p (*atm.*)	% He *at* 80°	% He *at* 70°
10	79	93
20	91	98
40	95·5	99·2
60	97·2	99·6
100	98·5	..

We see that, even at pressures as high as 100 atm., the highest purity obtainable at 80° is 98·5 per cent. He. Even apart from the fact that this high pressure is impracticable for other reasons, it is clear that at 80° pure helium cannot be obtained; for we cannot expect complete equilibrium to be reached. Evidently we must either use a refrigerant with a still lower temperature, or we must apply some additional method of purification, such as fractional adsorption on charcoal or the like. At 70° K., a temperature that can be maintained with liquid nitrogen boiling under reduced pressure, conditions are better. The table shows that pressures of about 40 atm. should be sufficient to obtain helium of 99 per cent. purity.

Thus low temperatures and fairly high pressures are required to produce pure helium from a mixture with nitrogen. But here another difficulty arises, owing to the solubility of helium in liquid nitrogen. As may be seen from Figs. 52 and 53, this solubility is not very great, especially at low temperatures, but we must remember that we are dealing with weak helium sources. When the original mixture contains only a small proportion of helium, a liquid containing a few tenths of a per cent. will already lead to considerable losses. Suppose the original mixture contained 2 per cent. He, 40 per cent. N_2, and 58 per cent. CH_4. Let us assume that we have removed all the methane in a fraction consisting of 90 per cent. CH_4 and 10 per cent. N_2 and no helium. The remaining gas, consisting only of nitrogen and helium, is then partially condensed, leaving a vapour containing 99 per cent. He. If the liquid fraction has 0·5 per cent. He dissolved in it, it means that 8·5 per cent. of the total helium present in the original mixture is wasted. The position becomes still more precarious when very weak mixtures are treated, and this is probably one of the reasons why these are not used in the United States. However, it has been possible to produce large quantities of pure helium from sources containing less than 0·3 per cent. He with very slight losses. This was achieved by a careful study of the separating process.

Dephlegmators and plate columns have been used to separate helium from nitrogen and methane and occasionally a combination of the two. There is apparently some uncertainty as to which are preferable, and the general opinion seems to be that, as the plate column is on the whole the stronger weapon, it should be applied in this rather difficult case. Actually the advantages of the plate column lie in its ability to separate substances whose boiling-points are close together, such as nitrogen and oxygen or nitrogen and carbon monoxide. For mixtures

with widely differing boiling-points, like nitrogen and helium, they have few advantages over dephlegmators. At first sight it might appear that they would be useful in preventing loss of helium dissolved in liquid nitrogen, but we shall see that this danger is smaller than might have been thought. A series of dephlegmators, correctly handled, are quite capable of producing helium of 99 per cent. purity with a very high yield, which precludes any extensive losses of helium through solution in liquid fractions.

Though the action of a dephlegmator has been described in Chapter III, using air as an example, it will be well to consider it again at this point, as applied to a mixture of nitrogen and helium. Suppose the mixture to be precooled in such a way that it enters the tubes of a dephlegmator from below as a saturated vapour. We assume that a suitable liquid refrigerant is boiling between the tubes. Then nitrogen will condense in the tubes and trickle down into the sump, as described in Chapter III. We have seen that the purity of the more volatile component, in our case helium, is determined by the temperature of the refrigerant. The highest purity obtainable is given by the composition of a saturated vapour at the given pressure and at the temperature of the refrigerant. In the case of oxygen–nitrogen mixtures, the purity of the nitrogen can be raised as high as we like. If the temperature of the refrigerant is below the boiling-point of nitrogen at the pressure of the mixture, and if the dephlegmator is sufficiently long, the nitrogen emitted at the top of the dephlegmator will be pure. In the case of helium–nitrogen mixtures, owing to the peculiar shape of the equilibrium curves at temperatures high above the critical temperature of helium, the purity is determined by the temperature and pressure according to Table 31 on p. 278. But the liquid collecting in the sump of the dephlegmator cannot contain less helium than is in equilibrium with the ingoing vapour. It will, in fact, always contain rather more than this amount.

Now consider a (T, x) diagram of helium–nitrogen mixtures, e.g. that for 20 atm. shown in Fig. 53. The mixture entering the dephlegmator will contain only a few per cent. of helium. The vapour curve is so flat that the composition of a liquid in equilibrium with any vapour will always lie close to the point where the two curves meet at a sharp angle; and the weaker the original helium–nitrogen mixture, the lower will be the helium concentration in the liquid. In the example given above of a 2 per cent. He source, the helium–nitrogen mixture obtained after removing the methane would contain 5·6 per cent. He. A liquid

in equilibrium with this vapour contains about 0·2 per cent. He, i.e. much less than the 0·5 per cent. that we assumed. And with a weaker mixture the losses would be proportionally smaller. It is thus clear that losses can be kept down by arranging for a suitable temperature of the incoming gas at the base of the dephlegmator, whereas to secure a high purity of the product, the temperature of the refrigerant between the tubes of the dephlegmator must be kept as low as possible.

In practice the separation of pure helium from mixtures containing methane and nitrogen is usually effected in two stages. In the first most of the methane and nitrogen is removed and the helium content is increased to anything between 5 and 30 per cent. This can be achieved at fairly low pressures of a few atmospheres. The rich mixture is thereupon warmed up and compressed to some 30 or 40 atm. and pure helium is then produced in the second stage.

The plant consists of a series of units, which may be dephlegmators or plate columns or an assortment of each. The original plant at Fort Worth, U.S.A., consisted mainly of plate columns, the Canadian plant at Calgary was a combination of plate columns and dephlegmators, and a plant in South Russia is composed of dephlegmators alone. Fig. 150 shows a typical dephlegmator plant.

The natural gas is compressed to the pressure necessary to supply the refrigeration, which will vary according to the size of the plant. It is then cooled and partially liquefied in two or more exchangers with cold returning vapours. Part of the gas is expanded in a cylinder behind the first heat-exchanger, the rest, together with the liquid already formed, is passed through a throttle valve. Liquid and vapour together thereupon enter the first dephlegmator (1) at an intermediate pressure. The uncondensed portion is then passed on to the second dephlegmator (2) and thence to the third (3). The liquid mixture of methane and nitrogen, collecting in the sump of (1), the composition of which will depend on that of the source, is expanded to atmospheric pressure and introduced between the tubes of (2), whence part of it overflows into (1). The liquid formed in the tubes of (2), which will consist mainly of nitrogen, is admitted after expansion between the tubes of (3). Almost pure liquid nitrogen, formed in the sump of (3), is added to the refrigerant supplied to (2). The refrigerants evaporating from all three units serve to cool and liquefy incoming gas. If the pressure of the mixture in the tubes of (3) is not far above 1 atm., the vapour escaping from the refrigerant is pumped off with a vacuum pump to lower the temperature. But if this pressure is maintained at 10 atm. or higher, this is not necessary.

In any case, the refrigerant in (1) is warmer than that in (2) and the latter is warmer than that in (3), since the methane content of the liquids decreases from one unit to the next. The rich gaseous $He–N_2$

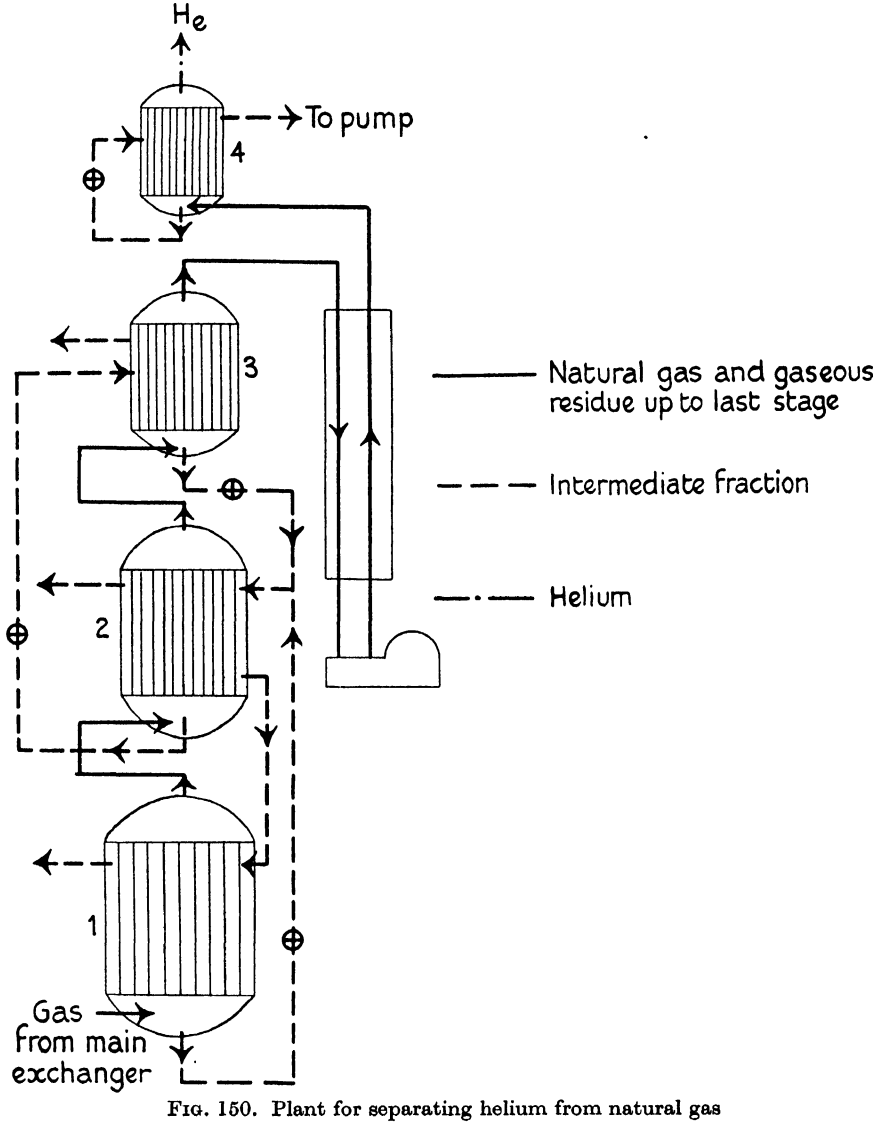


FIG. 150. Plant for separating helium from natural gas

mixture emerging from the summit of (3) may contain 5 per cent. He, as is the case in the corresponding unit of the Canadian plant, or 30 per cent. He, as in one of the Russian plants. This depends on the pressures at which this part of the apparatus is worked. The higher the pressure

in the tubes of the dephlegmators, the higher the helium content in the intermediate product and the smaller its quantity, i.e. the greater the achievement in the first stage of the process.

The enriched helium gas is now warmed up and recompressed to a pressure between 30 and 50 atm. It is then cooled down and partially liquefied in a series of exchangers and introduced into the sump of the fourth dephlegmator (4). The liquid is expanded to a pressure of one-quarter or one-fifth of an atm. abs., maintained by a strong vacuum pump, and admitted between the tubes of (4), where it boils at a temperature which may be as low as −207° C. (66° K.). The final product, emerging at the top of (4), has a helium content that varies from 97 to 99 per cent., according to the dimensions of the dephlegmator and the pressures inside and outside the tubes.

The dephlegmators become smaller and smaller as the separation proceeds, and the product of (4) is so small that it is not worth while passing it through the exchangers.

XII

THE SEPARATION OF OLEFINES FROM CRACKER GAS

1. The principles of separation

THE cracking of oil, with a view to increasing the quantity and improving the quality of the petrol fraction has added very materially to the world resources of combustible gas. About 20 per cent. by weight of the petrol produced is emitted as gas, most of which is used for industrial heating on the spot or passed into the gas mains. As much as 80 per cent. of heavy oil can be converted into petrol by cracking. Almost 10^{10} gallons of petrol are produced annually by cracking in the U.S.A. together with about 3×10^{11} cu. ft. of gas. The annual production of cracker gas is thus not far behind that of coal and coke-oven gas.

The composition of cracker gas differs considerably according to the conditions of pressure and temperature in the cracking plant and according to the properties of the crude oil. But in every case the composition is very different from that of the gases hitherto discussed. Cracker gas is characterized by a high percentage of unsaturated hydrocarbons of the olefine series and the absence of carbon monoxide and nitrogen. Cracker gas is essentially a mixture of hydrogen and hydrocarbons. Industrially, the importance of cracker gas lies in its high olefine content, since olefines are growing more and more valuable as basic substances for chemical synthesis. The production of pure olefines from cracker gas is therefore rapidly becoming an important large-scale industry.

In recent years several new types of cracking processes have been developed, the primary object of which is no longer the production of petrol or in fact, of fuel at all, but in which certain oil fractions such as gas oil or naphtha are cracked with a view to obtaining valuable chemicals. These processes, which are often of a catalytic nature, are so conducted as to convert the greatest possible portion of the raw material into certain groups of hydrocarbons, among which light and heavy olefines, as well as aromatic compounds, play an important part. Under these conditions the cracker gases cease to be a more or less subsidiary by-product and, in view of their high olefine content, their production in suitable quantities and with the desired composition becomes one of the main objects of the process itself. At present several such plants are under construction in this country.

The production of olefines from cracker gas is the most intricate

problem of industrial gas-separation. Though it is carried out according to the same principles as the processes already discussed, it necessitates the use of rather complicated plant, giving rise to involved flow-sheets. The difficulties encountered are due to three main causes.

1. Cracker gas is not even approximately a binary system. As can be seen from Table 7, p. 7, it contains five or six constituents in percentages from 6 to 30. None of these can reasonably be neglected, even for rough calculations.
2. Whereas hitherto, with the exception of argon, we were always interested in those components of a mixture with the highest or lowest boiling-points, we are here seeking to separate off components with intermediate boiling-points. Those of ethylene and propylene are higher than those of methane and hydrogen and lower than those of propane, butane, etc.
3. If we arrange the constituents of cracker gas in the order of their boiling-points, there are always one or more paraffins between two olefines. Thus the boiling-point of ethane lies between those of ethylene and propylene. Propane and iso-butane lie between propylene and the butylenes, etc. It is therefore not possible to obtain fractions from cracker gas containing olefines only and then to separate the olefines from one another. There is always an intervening paraffin to complicate the process. This is illustrated in Table 26, p. 259.

The separation of cracker gas with a view to obtaining pure olefines is therefore difficult, alike from a practical and from a theoretical point of view. It has been taken up first, as was to be expected, in the U.S.A. and the U.S.S.R., the two principal oil-producing countries having at the same time a highly developed chemical industry. A large number of processes have been devised, which differ very considerably from one another. These differences refer to the type of fractions produced and to the sources of refrigeration employed; moreover, the details of the plant naturally depend on whether ethylene only is to be obtained, or whether pure propylene and higher olefines are also desired.

Every low-temperature plant for the separation of cracker gases consists essentially of a number of fractionating columns with suitable refrigerating equipment, involving compressors and heat-exchangers for treating the gas itself as well as any refrigerants used in the process. There are, however, several possible variants as may be inferred from the following considerations.

1. *Temperatures and pressures.* In view of the low boiling-points of the hydrocarbons listed in Table 26, the separation of cracker gas by distillation at atmospheric pressure would require very low temperatures. On the other hand, by compressing the gas the boiling-points of the constituents can be raised and the temperatures required for separation will be correspondingly higher. However, quite apart from the cost of compression to very high pressures, the procedure is limited by the critical pressures and temperatures of the components. Above the critical curve the two-phase equilibrium necessary for a fractionation process cannot be brought about at all, and it was shown in Chapter II that on approaching critical conditions the dew- and boiling-curves move closer together and separation becomes more difficult. Since the critical points of methane and ethylene are both below room-temperature and that of ethane at 32° C. is only just above, it is clearly not possible to effect a complete separation of cracker gas by distillation without any refrigeration at all.

Nevertheless, there are two ways of approaching the problem. We can either keep the pressure low and accept very low temperatures, or we can raise the pressure of the cracker gas and work at higher temperatures involving less refrigeration. Experience has shown that the power consumption can be much the same in both cases; in one, more power is expended on compressing the gas and less on compressing refrigerants; in the other case the position is reversed.

2. *Refrigerant cycles.* There has been a general tendency in the separation of cracker gas to work at fairly high pressures and temperatures. This is partly due to the fact that the processes have been developed for the oil industry which is not accustomed to the use of low temperatures and which sees the separation of the lower hydrocarbons as a continuation of the normal distillation customary in the industry. When dealing with hydrocarbons containing less than four carbon atoms it was found expedient to replace the cooling water normally used to condense the column reflux by a refrigerant such as ammonia or propane, boiling at slightly elevated pressures at around −30° C. For some problems of cracker-gas separation, this mild form of refrigeration was found adequate, though it often necessitated considerable compression of the gas itself. In most cases it was necessary to go to rather lower temperatures and ethylene was used as an additional refrigerant. Sometimes even this was not enough and a further methane cycle was introduced.

Almost every cracker-gas separation plant requires at least two

fractionating columns. If more than two are used, two of them generally need a cold reflux, and condensation will take place at different temperatures in the two condensers. Since refrigeration is thus required at various levels, it is almost always economical to use two refrigerants or at least one refrigerant boiling at different pressures, rather than to supply all the refrigeration at the lowest temperature at

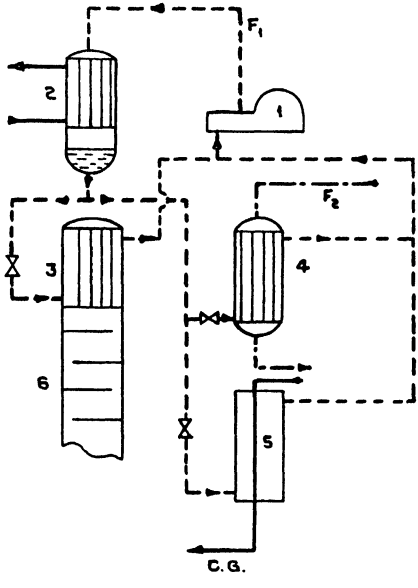


FIG. 151. Functions of refrigerant in cracker-gas separating plant
After compression in the compressor 1 and liquefaction in the water-cooled condenser 2, the refrigerant F_1 performs three duties. One part provides reflux for the column 6 by evaporating in the reflux condenser 3, a second part liquefies another refrigerant F_2 in the condenser 4, and a third part cools and partially liquefies cracker gas in the exchanger 5

which cold is required. When two refrigerants are employed, it is advantageous to use them in 'cascade', condensing the refrigerant with the lower boiling-point under pressure in thermal contact with the other refrigerant boiling at atmospheric pressure. The same arrangement can be used when more than two refrigerants are circulated.

Thus one or more refrigerants can serve a multiple purpose; they can supply reflux to fractionating columns with cold overheads and they can serve to condense other refrigerants with lower boiling-points than themselves. They can also perform a further function by precooling and partially condensing the cracker gas itself. This is illustrated in Fig. 151.

3. *Cracker-gas fractions and foreign refrigerants.* The refrigerants

referred to above are circulated in closed cycles and do not come into direct contact with the cracker gas itself. If propane or propylene is used in the first cycle instead of the more conventional ammonia, it is because both are readily available as components of the cracker gas. The second refrigerant is generally ethylene or ethane for the same reason and because they are the most suitable refrigerating agents for the required temperatures.

If ethylene serves as a refrigerant to provide reflux in a column yielding pure ethylene as overhead product, it is possible to omit the reflux condenser altogether and to inject the liquid ethylene directly on to the top plate of the column, as was described in Chapter XI, where the advantages and disadvantages of this procedure were discussed. Similar conditions can apply in a column producing a propylene overhead. In these cases a part of the overhead is subsequently withdrawn and re-compressed as refrigerant and is thus separated from the product.

It will readily be seen that this procedure, if taken to its logical conclusion, can lead to the disappearance of independent refrigerating cycles altogether. It is not essential to provide 'foreign' refrigerants for the separation of cracker gas at low temperatures. The necessary refrigeration can be supplied by re-compressing and re-cycling the products of the separation process or even some of the impure fractions of the cracker gas itself. Plants of this type have been built and frequently appear in the patent literature.

Since the re-boilers of some of the columns operate well below the surrounding temperature, it is natural to supply the required heat by condensing in them those refrigerants or evaporated cracker-gas fractions that boil at suitable temperatures.

4. *The effect of cracker-gas composition.* In comparing certain processes for the separation of cracker gases, the differences in the composition of these gases are sometimes overlooked. According to the type of cracking process employed and to the nature of the charge stock, the gas composition varies very considerably and the gas-separation plant must vary accordingly. Not only can the olefine content vary from 10 to 40 mole per cent. of the feed gas, but the amounts of hydrogen and methane can also vary between very wide limits. The following table shows the composition of two typical cracker gases, the separation of which was undertaken recently.

These two gases are at first sight fairly similar, but it will be noted that the C–3 fraction is three times as great in the first gas as in the

TABLE 32. *Composition of two typical cracker gases*

	Gas I *Mol %*	*Gas II* *Mol %*
Hydrogen	11·5	9·3
Methane	16·5	43·8
Ethylene	19·4	21·1
Ethane	17·7	11·2
Propylene	8·9	10·7
Propane	24·0	1·2
C–4's	1·5	2·3
C–5's	0·5	0·4

second and the methane content nearly three times as great in the second as in the first. In particular the amount of 'tail gas', i.e. of hydrogen and methane together, is 28 per cent. in Gas I and 53 per cent. in Gas II.

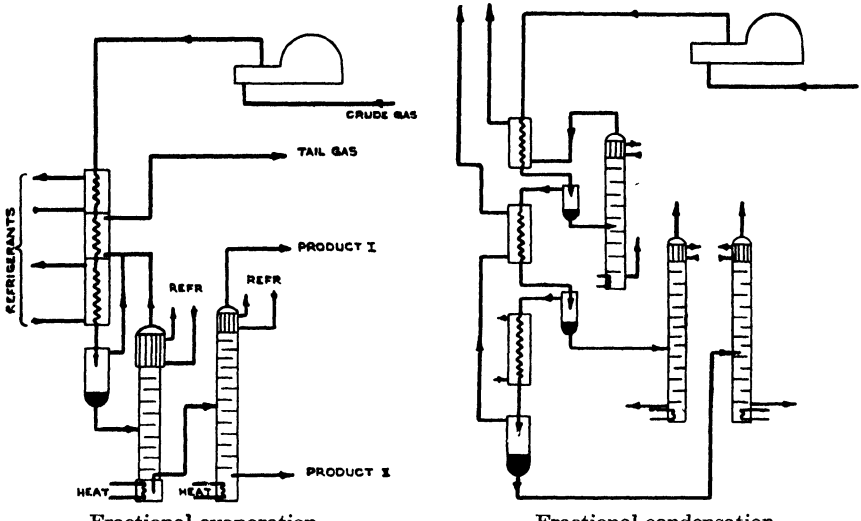
Suppose that it is desired to produce fairly pure ethylene from both these gases. Then at some stage of the process it will be necessary to separate the ethylene from the lower-boiling constituents methane and hydrogen. To do this, the whole or a part of the original gas must be separated into a liquid and a gaseous portion, the former containing almost all the ethylene and the latter containing methane and hydrogen but very little ethylene. Now if the initial mixture is progressively cooled until most of the ethylene is liquefied, a part of the methane will condense also. At a given pressure the temperature at which substantially all the ethylene has passed into the liquid phase will depend primarily on the methane and hydrogen content. The more methane and hydrogen are present in the gas, the lower will be the temperature to which it must be cooled to condense the ethylene.

In the case of the two gases listed above, if a pressure of 10 atm. is chosen, it can be shown with the help of the equilibrium ratios discussed in Chapter II that a 90 per cent. recovery of ethylene requires a temperature of −80° C. for Gas I and −100° C. for Gas II, provided that the whole of the raw material is cooled down together. Moreover, in both cases nearly half the methane has to be condensed to secure a 90 per cent. ethylene recovery.

5. *Fractional condensation and evaporation.* In the example just mentioned it was assumed that the process was conducted as follows: the cracker gas, compressed to a suitable pressure, is cooled down until all the constituents with boiling-points higher than that of methane are in the liquid phase. As we have seen, this involves the condensation of a large part of the methane also. The remaining 'tail-gas' consisting substantially of methane and hydrogen, is then removed, and the liquid is

fractionated in a number of columns to yield the required pure products. This method may be termed 'fractional evaporation'. All the intended products are first liquefied in one operation and then 'fractionally' evaporated.

Another form of process, which may be termed 'fractional condensation', operates rather differently. At some temperature much higher than that needed to condense virtually all the ethylene, a condition is



Fractional evaporation Fractional condensation

FIG. 152

reached at which nearly all the propylene is in the liquid state. At a still higher temperature all the C–4 hydrocarbons will condense. It is thus possible to withdraw liquid fractions at successive temperatures as condensation proceeds, and to separate these into pure components without cooling all the raw material to the lowest temperature. Fig. 152 illustrates the two processes schematically.

The latter method offers certain advantages as it is not always possible to recover all the cold used to cool the condensed gases far below their condensation points. However, it has the following disadvantage. If separate C–4, C–3, and C–2 fractions are drawn off during condensation, in such a way that the C–3 fraction contains virtually no C–4 hydrocarbons and the C–2 fraction virtually no C–3's, it will in general be found that considerable quantities of C–3 hydrocarbons will condense with the C–4's and some C–2's will appear in the C–3 fraction. In the terms of the distillation industry, it is not possible to obtain a 'clean cut', C–3's and C–2's will therefore each be present in two fractions

and the final C–3 product will be made up from two subsequent fractionating operations, the C–3's appearing as overhead from one column and as 'bottoms' from another. This leads to a complication of the fractionating process.

6. *The effect of mutual solubility.* Fractional condensation has a further disadvantage connected with the mutual solubility of the components. For every mixture of hydrocarbons every pressure will have a corresponding temperature at which a large proportion, say 95 per cent., of a certain hydrocarbon will be contained in the liquid phase. We have already seen in (5) how this temperature depends on the hydrogen content and on that of methane, the most volatile hydrocarbon. But the less volatile components also exert some influence on this temperature. It can be shown with the help of the equilibrium K-values that the presence of heavy components in the liquid facilitates the condensation of the lighter components, thus raising the temperature at which, under the given pressure, the condensation of a given component is 95 per cent. This simply means that light hydrocarbons are, to a certain extent, soluble in heavier hydrocarbons; or that every process of partial condensation is also an absorption process.

Now the withdrawal of intermediate liquid fractions in the course of partial condensation at progressively lower temperatures involves a successive removal of heavier components from the mixture and thus impedes the absorption of light hydrocarbons. The result is that the temperature at which 95 per cent. of the given component condenses is lower than it would have been if no liquid had previously been withdrawn. Thus, from the point of view of obtaining the required initial-phase separation at as high a temperature, or at as low a pressure as possible, it is advisable not to withdraw liquid fractions from the mixture in the course of the partial condensation stage of the process.

7. *The use of dephlegmators.* The difficulty of obtaining a 'clean cut' by the partial condensation of cracker gas complicates the separation process and adds materially to its cost. In particular if ethylene is to be produced from a gas containing very much more methane than ethylene, partial condensation, if carried to a point at which virtually all the ethylene is liquefied leads, as we have seen, to the condensation of large quantities of methane also. All this methane has ultimately to be re-evaporated and this generally occurs in a fractionating (stripping) column which requires a liquid methane reflux to prevent loss of ethylene. However this reflux is supplied, it involves the use of low-temperature refrigeration and is therefore expensive.

To reduce the amount of low-temperature cold required to condense unwanted constituents and subsequently to strip the liquid fractions, both the German Linde Company and the American Air Reduction Company have made extensive use of dephlegmators in the partial condensation stage of the process. By passing the condensing gas through a dephlegmator cooled with a low-temperature refrigerant, a much cleaner cut is obtained than is possible in a normal condenser and the separation of ethylene from methane and hydrogen can be substantially accomplished in a single step. It must, however, be noted that this device does not eliminate the need for low-temperature cold, but merely reduces it somewhat. Moreover, the cut so obtained is not generally quite clean enough and a certain amount of subsequent stripping has to follow. There is some difference of opinion as to how far the use of dephlegmators does in fact improve the separation process.

2. Separating plants for cracker gas

We shall first consider a Russian plant, built as long ago as 1935, using foreign refrigerants. Separation is effected at 30 and 25 atm. in two rectifying columns. The refrigerants used are ammonia, boiling at reduced pressure, and a closed ethylene cycle, as well as liquid ethylene obtained in the separation process. The plant is actually used to produce ethylene, propylene, and higher olefines, but we shall discuss only the parts for separating ethylene.

The process is shown schematically in Fig. 153, in which the compressor and purification plant have been omitted. We assume that moisture and traces of carbon dioxide, as well as small quantities of benzene and toluene, have been removed.

The cracker gas, compressed to 30 atm., first traverses the main heat-exchanger E_1, in which it is cooled by all three outgoing products —a mixture of methane and hydrogen, almost pure ethylene, and a residue consisting of components with higher boiling-points than ethylene. It is then further cooled in the ammonia heat-exchanger N and in an additional heat-exchanger E_2 in counter-current with the methane–hydrogen mixture.

The compressed gas leaves E_2 at about $-50°$ C. and is admitted, partially liquid, to the middle of the 'cold column' C, in which methane and hydrogen are removed from it. The column has two condensers in series, shown in the figure separately and distinct from the column. The first K_1 is fed with liquid ethylene from the closed ethylene cycle (not shown in the figure), the second K_2 with liquid ethylene obtained

from the cracker gas. The temperature of the condensed reflux returned from the condensers is about −90° C. The reboiler at the bottom of the column *C* is heated with an external source to +10° C. The vapour leaving the summit of *C* is a mixture of hydrogen and methane; the liquid returned from the condensers is almost pure

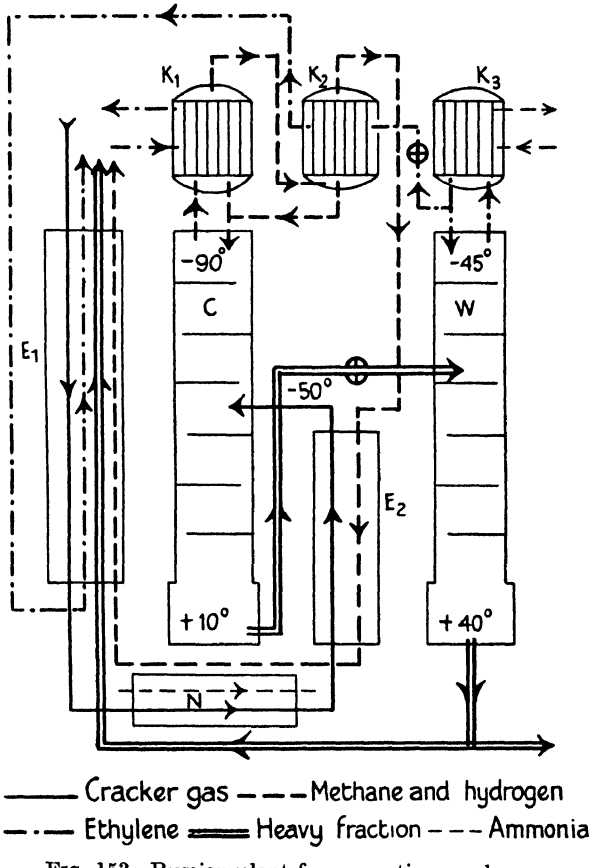


FIG. 153. Russian plant for separating cracker gas

methane. It serves to scrub out ethylene from the rising vapours. As no methane leaves the column except from the top, the effluent ultimately leaving K_2 and returned through E_2 and E_1 contains the same ratio of methane to hydrogen as the original mixture (about 2·2:1). But in view of the condensation of methane in the condensers and its readmission to the column, its concentration in the upper part of the column, under stationary conditions, is very high. Even so the effluent still contains 2–3 per cent. C_2H_4, which is thus lost in the process.

The liquid fraction collecting in the sump of the column C, which contains all the rest of the ethylene and practically no methane or hydrogen, is expanded from 30 to 25 atm. in a valve and then admitted to the middle of the 'warm column' W. The condenser K_3 of this column is fed with liquid ammonia boiling at reduced pressure at a temperature of about $-45°$ C. The sump is heated with steam to $+40°$ C. In W the fraction is separated into a vapour consisting of 99 per cent. C_2H_4 and a liquid consisting of all the components with boiling-points above that of ethylene together with about 2 per cent. C_2H_4, which is lost. Part of the ethylene liquefied in K_3 is readmitted as reflux to W and serves to scrub out ethane and higher hydrocarbons; the rest is transferred as refrigerant to K_2, after being expanded to atmospheric pressure. The ethylene vapour evaporating from K_2 is withdrawn through the main heat-exchanger E_1.

The liquid fraction formed in the sump of W is either returned directly through E_1, or is transferred to a third column (not shown in the figure) for the separation of propylene.

In this plant the ethylene yield is about 85 per cent. The method is essentially fractional evaporation. The use of liquid methane as a refrigerant for providing reflux in the cold column is avoided by working at a relatively high pressure (60 per cent. of the critical pressure of ethylene). As a result the flow-sheet is simple but the yield not very high.

Very similar plants have been built more recently in the United States and are described by Pratt and Foskett.† The pressure in this case is as high as 40 atm. A plant recently erected in England follows similar principles but works at much lower pressure and correspondingly lower temperatures.

The development of this method to yield other products with boiling-points higher than that of ethylene does not involve any new principles but merely leads to further columns and more complex refrigeration cycles in order to provide cold reflux and reboiler heat in cold columns.

In Fig. 154, which shows the general principles, the gas compressor is followed by several aftercoolers and a dryer D, which may conveniently operate at a temperature somewhat lower than the surroundings. A certain amount of condensate C is usually drawn off before the dryers, consisting of heavy hydrocarbons, impurities, and water.

The gas is then cooled and partially condensed and the two phases are separated in the vessel S. If ethylene is to be one of the products, the

† A. W. Pratt and N. L. Foskett, *Am. Inst. Chem. Eng.*, p. 149 (1946).

liquid in S will have to contain almost all the ethylene in the original mixture, together with some methane. This is stripped off in the first column. In the second column a C–2 fraction can be withdrawn as overhead and separated into pure ethylene and ethane in a further column, as indicated in the figure. Alternatively the second column can yield pure ethylene and the third pure ethane.

In view of the proximity of the propane and propylene boiling-points, the next column will generally produce a C–3 fraction as overhead, which can be further separated if desired. The bottoms from this

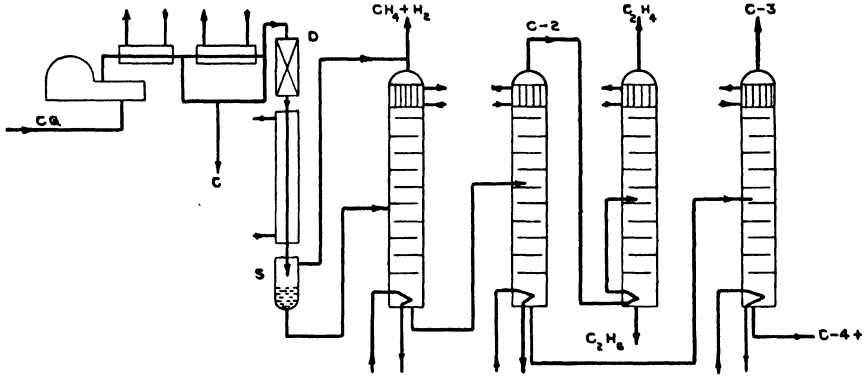


FIG. 154. Schematic cracker-gas separating plant

column will contain C–4 hydrocarbons and possibly some C–5's and C–6's depending on the composition of the original mixture. A further column may be added for the separation of this fraction, but this will probably operate above room-temperature.

Refrigeration and recovery of cold have been left open in the schematic figure, as some of the many possibilities have been discussed above. The cold available in the returning products will clearly be utilized, though it is not always easy to achieve this. Refrigeration will be required to cool and partially condense the gas and to provide reflux for the columns. Low-temperature heat will be needed in the reboilers. Heat and cold have to be provided at a number of different levels and these will again depend on the composition of the mixture and on the delivery pressure of the compressor. The most economical combination will be different in every case and plenty of scope is left to the design engineer in the choice of a solution.

As an example of 'fractional condensation', one of the older plants patented by the Air Reduction Co. in 1934, may be briefly described.

No foreign refrigerants are used in this plant, which is illustrated in Fig. 155.

It consists in the main of two plate columns C and W, each of which is divided into two parts by a condenser in the middle. A dephlegmator

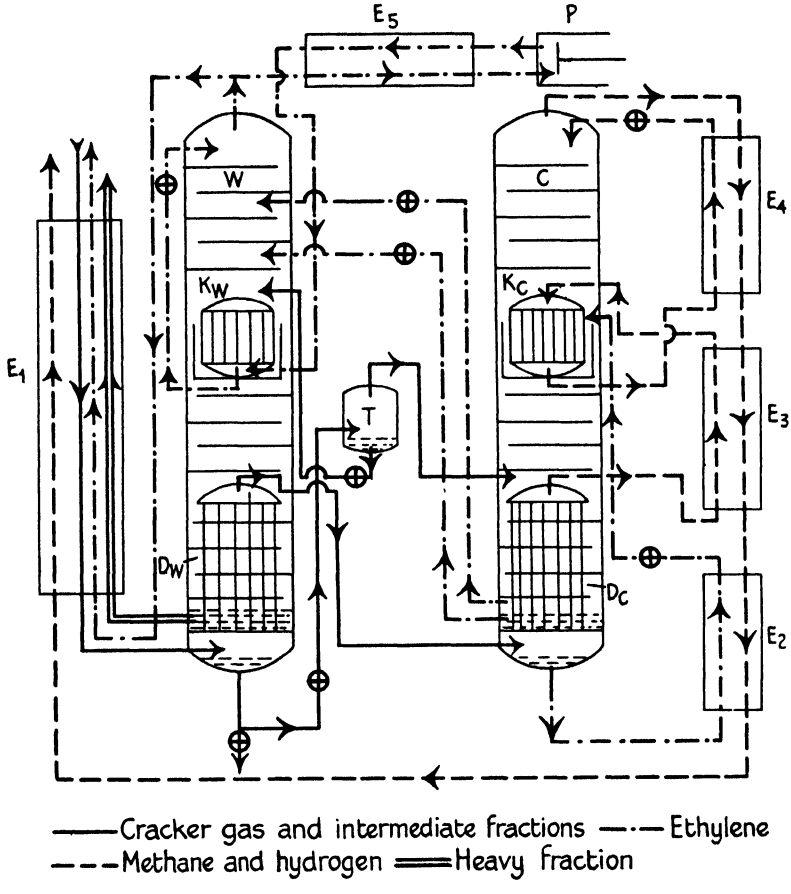


FIG. 155. American plant for separating cracker gas

is inserted at the bottom of each column, surrounded by baffle trays of the type described in Chapter III, p. 73.

After passing through the main heat-exchanger E_1, in which it is cooled by all three products, as in the previous plant, the compressed cracker gas is admitted at the bottom of the dephlegmator D_w of the column W, where it is partially condensed with the help of a fraction to be described later. In D_w a preliminary separation occurs, which is not assumed to be very effective. The liquid fraction consists essentially

of ethylene and constituents with higher boiling-points, and the effluent contains ethylene and more volatile components. But small quantities of methane may be dissolved in the liquid and small quantities of ethane may remain in the vapour.

The liquid fraction is expanded to an intermediate pressure into the trap T, in the course of which part evaporates, including all the methane. The liquid residue is expanded to approximately atmospheric pressure and delivered near the bottom of the upper section of the column W. It now consists only of ethylene and constituents of higher boiling-points.

The vapour withdrawn from the top of D_w is transferred, still at high pressure, to the bottom of the dephlegmator D_c in column C. Here it is separated into a vapour consisting only of methane and hydrogen, and a liquid fraction containing ethylene and small traces of components with higher and lower boiling-points. The liquid is sub-cooled in an exchanger E_2 with the help of cold hydrogen–methane vapour, expanded to an intermediate pressure, and admitted to the bath around condenser K_c in C. From here part of it flows over into the lower part of C, passes over the lower plates, and trickles down the baffle trays, finally collecting around D_c. This liquid fraction has now lost all traces of methane and consists of ethylene with small amounts of less volatile components.

Liquid and vapour from the bottom of C are expanded to low pressure and introduced in the middle of W above the fraction already described.

In this way, all fractions containing ethylene and less volatile components are united in W, the methane and hydrogen having been removed. To complete the separation of ethylene, two processes are still required: the constituents with higher boiling-points must be scrubbed out of the ethylene in W, and the ethylene itself must be scrubbed out of the methane–hydrogen effluent in C. For this purpose a reflux of liquid ethylene must be supplied at the top of W and a reflux of liquid methane at the top of C.

The ethylene reflux is obtained as follows. Part of the ethylene effluent from W is branched off before the main heat-exchanger E_1 and warmed up to room-temperature in an exchanger E_5. It is then compressed to about 100 atm. in the compressor P, cooled again in the same exchanger E_5, and liquefied in the condenser K_w in W with the help of the fraction transferred from the sump. The liquid, which should be very pure ethylene, is expanded to 1 atm. and admitted at the top

of W. The final effluent from W, apart from the recompressed portion, is withdrawn through E_1. The function of the compressor is to supply additional refrigeration and thus to replace the ethylene and ammonia cycles, used in the plant described previously.

The methane reflux is obtained by condensing part of the hydrogen–methane effluent from D_c in the condenser K_c in C, after cooling it in an exchanger E_3 with the help of cold hydrogen–methane vapour. It is then further cooled in E_4, expanded to the intermediate pressure obtaining in C, and admitted at the top of the column. The effluent from C, consisting of methane and hydrogen only, is returned through E_4, E_3, and E_2, and finally through the main heat-exchanger E_1.

The purity of the ethylene obtained from this plant is given as 99 per cent. We have no information as to the yield, but it is probably slightly higher than that of the Russian plant.

This flow-sheet clearly shows the difficulties inherent in the fractional condensation method. The simple cut, envisaged as the initial stage of separation, is evidently not possible in a dephlegmator. We cannot separate in this way a gaseous phase containing only ethylene, methane, and hydrogen, and a liquid phase containing only ethylene and less volatile components. The insertion of the trap T indicates that some methane is present in the heavier fraction, and the readmission of liquid ethylene in the centre of the upper part of W shows that it contains a certain amount of ethane. The difficulty of separating ethylene and ethane is clear from the shape of the equilibrium curves of the ternary methane–ethylene–ethane system in Fig. 47. Here most of the liquid curves are almost horizontal and the connodals fairly symmetrical about the methane axis.

The most characteristic point in the plant is the transfer of the liquid fraction from C to W. The final purification of the ethylene is carried out in the presence of *all* the constituents with higher boiling-points in a single process, after all the methane and hydrogen have been removed in C. Moreover, just as no foreign refrigerants are required, no external heating is needed in this plant. Since the pressure in the column W is near to 1 atm., the temperature at which the final separation of ethylene occurs is much lower than in the other plant. All the heat required is supplied by the condensing fractions in D_w, D_c, K_w, and K_c.

Finally, let us consider an American plant for separating ethylene and propylene from cracker gas simultaneously. The process was developed by the Air Reduction Co. and patented in 1936. As in the plant last described, no foreign refrigerants are used; the refrigeration

required is obtained by recompressing gaseous fractions and, in one case, expanding gas in a cylinder.

The essential feature of this plant is the simultaneous production of two liquid fractions and a gaseous effluent in the initial stage of separa-

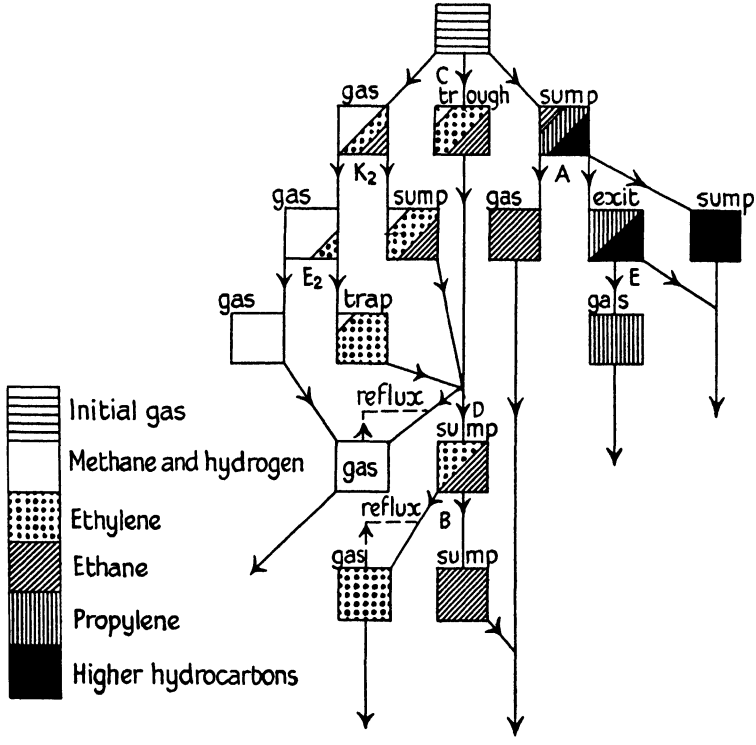


FIG. 156. Diagram showing stages of separation in American cracker-gas plant

tion. One fraction contains all the propylene and no ethylene, the other no propylene and the major part of the ethylene. The rest of the ethylene, with some ethane, escapes temporarily with the gaseous effluent. The cut between the two liquid phases is thus effected through the ethane, which is contained in both fractions. This is facilitated by the use of a rectifying column in the initial stage, as against the dephlegmator used in the last case. A plate column allows sharper cuts to be made than are possible in other types of apparatus.

The process is illustrated diagrammatically in Fig. 156 and the flow-sheet is shown in Fig. 157.

The cracker gas, compressed to about 12 atm., after traversing the main heat-exchanger E_1, in which it is partially liquefied, enters the

middle of the lower part of column C, which is fitted with an evaporator and a condenser K_1. One liquid fraction collects in the sump, the other in a trough under the condenser. All the ethylene is contained in the

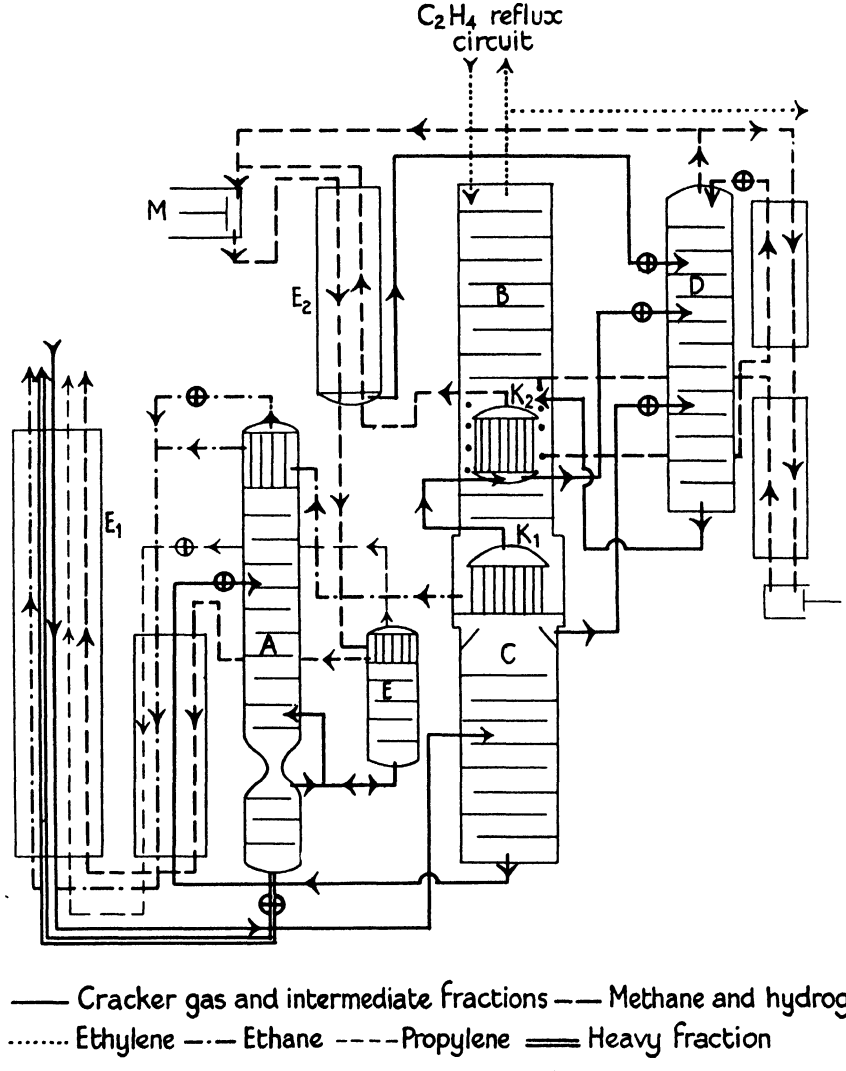


FIG. 157. American plant for separating cracker gas

latter fraction and the effluent; all the propylene in the sump. The overhead is freed of ethylene in the condenser K_2 and finally in an exchanger E_2, in which it is cooled by the methane–hydrogen mixture which has traversed the expansion engine M.

At this stage the following phases have been separated:

a liquid fraction containing all the propylene and no ethylene;
a gas containing neither ethylene nor propylene;
three liquid fractions containing together all the ethylene and no propylene (one in the trough of C, one in the sump of K_2, and one in a trap under E_2).

These three fractions are thereupon united in the auxiliary column D, provided with a reflux of liquid methane, and are thus separated into a liquid fraction containing only ethylene and ethane and an overhead containing only methane and hydrogen. This gas is united with the effluent from K_2, and we now have

a liquid containing all the propylene and no ethylene;
a gas containing neither ethylene nor propylene;
a liquid containing all the ethylene and some ethane.

This last liquid is rectified in the column B above C, where it is provided with a reflux of liquid ethylene. It results in the final separation of all the ethylene. The methane and ethylene refluxes are obtained by recompression and cooling of the products. In this way the original effluent and the liquid formed in the trough of C have been separated into three parts:

(1) hydrogen and methane;
(2) ethylene;
(3) ethane.

The propylene fraction is separated in the auxiliary columns A and E into the following corresponding parts:

(1) ethane;
(2) propylene;
(3) propane, butylenes, etc.

It is unnecessary to go into further detail in discussing the plant, as it is described in the patent specification merely as an example and is obviously capable of a number of variations.

3. Other methods of cracker-gas separation

Before the development of low-temperature methods for cracker-gas separation, C–3 and C–4 hydrocarbons were frequently recovered from these gases by absorption in oils at ordinary temperatures and elevated pressures and subsequent stripping of the oil at higher temperatures. The amount of gas soluble in suitable oil decreases with the normal

boiling-point of the gas, and hence the amount of oil that has to be circulated to achieve a high recovery becomes very great when dealing with the lightest hydrocarbons. For butenes and propylene the method is quite economical, but it is hardly possible to attain a reasonable recovery of ethylene by oil absorption alone. In some cases other absorbents have been used successfully which cause the olefines to be bound chemically.

In the running costs of absorption processes, as compared with low-temperature methods, power is largely replaced by the heat needed to strip the absorbents. The economics of the two processes are therefore governed by the relative cost of heat and power, which differs considerably from one country to another and according to conditions in a particular factory. A further important item is the extent of the required recovery. In the United States, where cracker gas is available in almost unlimited quantities, a high yield of products is not generally important, and in this case oil absorption methods can be very useful. In Great Britain and on the European continent the supply of cracker gas is small, and in some cases the gas is produced expressly for the sake of the olefines which it contains. Under these conditions a high yield is vital and it would be uneconomical not to recover the bulk of the ethylene. In general, oil absorption is not suitable for application in this country.

Greater importance must be attached to a method recently developed by the Union Oil Co. of California which makes use of adsorption on activated carbon. The 'vapour-pressure curves' of adsorbed gases, i.e. the relation between adsorption pressure and temperature for a constant quantity of adsorbate, are steeper than the vapour-pressure curves of pure liquids, and the corresponding 'relative volatilities' differ more from one gas to another. Equilibrium ratios can be defined for adsorption equilibria similar to the 'K-values' for liquid–vapour equilibrium, and the resulting K's will show a stronger differentiation than in the latter case. Separation by adsorption and desorption is therefore not only possible but in principle more efficient than by making use of liquid–vapour equilibrium.

Until recently the main difficulty in using this method was dealing with solid substances that required alternate heating and cooling. As long as the adsorbent remained in a fixed position, only batch processes could be used, which were uneconomical for treating large quantities.

In the Hypersorption Process the carbon bed is moved slowly down a column in counter-current to the gas which is to be separated,

adsorbing gas in a low-temperature zone and desorbing at higher temperatures. A process very similar to fractionation takes place in the column. The results of laboratory and pilot-plant work, which have been described by Berg† show that the method is applicable to C–2 compounds as well as to those with higher boiling-points and can even be used for separating hydrogen and methane. A number of technical difficulties have to be overcome, such as the formation of carbon dust by abrasion of the particles, but the process has already led to important developments in the separation of low-boiling hydrocarbon mixtures. In a plant at Michigan which was started up in 1947, ethylene is recovered from 'tail gas' consisting mainly of hydrogen and methane, and containing 6 per cent. C_2H_4. The ethylene yield of this plant is 98 per cent. and the product has an ethylene content of 93 per cent., the remainder being essentially acetylene and carbon dioxide. The plant treats 2,000 m.^{3} of gas per hour and 8 tons/hr. of carbon are circulated.‡

† C. Berg, *Amer. Inst. Chem. Eng.* **42**, 665 (1946).

‡ H. Kehde, R. G. Fairfield, J. C. Frank, and L. W. Zahnstecher, *Chemical Engineering Progress*, **44**, 575 (1948).

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