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PHYSICAL BASIS OF SEPARATING HELIUM AND NITROGEN

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In this article determinations are given for diagrams of p - x - mixtures of helium-nitrogen under pressure of 5 to 150 atm and at temperatures of 64, 78, 90 and $108^{\circ}K$ and diagrams of T-x at 4 and 20 atm. Calculations are given for i-x-diagrams for pressures of 4 and 20 atm on the basis of T-x-diagrams.

The purpose of this study was to solve the problem of obtaining pure helium from natural gases with the least possible losses of helium. Since all admixtures with the exception of N_2 were easily removed from natural gases, we had to deal mainly with a binary admixture H_e - N_2. In order to select the means of obtaining helium of sufficient purity and reducing its losses to a minimum, it was necessary to study the equilibrium curves of this mixture when the method of deep cooling was used.

Separation of the gaseous mixture by means of deep cooling required the use of various methods, depending on the proportions of component concentrations and on the intervals of their boiling points. When the value of the concentrations was of the same order and the boiling points were far apart from one another, it was possible to attain good results by means of a partial reduction of the mixture in the condenser or in the tubes. Admixtures of components in gaseous phase having higher and

lower boiling points, as well as the solubility of the latter in a liquid, may be lowered to a tolerable limit. If the boiling points differed slightly in analogous concentrations then it was advantageous to use the method of rectification in which the two phases merged in the column, and in which the liquid was concentrated by the higher boiling, and the gas by the lower boiling component. When the concentrations of both substances were drastically different, new difficulties arose during their separation, which also differed, depending on whether the component under study had a lower or higher boiling point.

Due to the efforts of Dodge and Dunbar [1], Merkel [2], Wiseberg [3] and others, the process of rectification of air and the calculation data might be considered to be sufficiently developed. Otherwise, we would have had to deal with those mixtures whose boiling points were far apart from each other, especially in those instances where the separation had to be performed over the critical temperatures of one of the components and, because of the small concentration of this component, partial condensation became impractical. In the case of a gaseous mixture He - N_2 in which the boiling points were far apart from each other and the concentration of helium was small in comparison with nitrogen, we had to study the equilibrium curves of this mixture over varying pressures and various temperatures so as to be able to select the most appropriate conditions for separation.

We examined equilibrium curves of He - N_2 mixture under static as well as dynamic conditions. For static conditions we used a device (Fig. 1) which was immersed in liquid nitrogen or in nitrogen under

evacuation. The incoming mixture with 60% helium passed through a valve and a spiral tube from the cylinder into the device in which separation occurred. A mixer E was inside the device, and mixed the liquid phase. Analyses of the liquid phase were taken through lower tube A, and those of the gaseous phase through the upper tube B. The two phases expanded to atmospheric pressure in the valves which were at room temperature, following which they were passed through the analyzer. For analysis we used an analyzer based on the principle of heat conductivity included in the Wheatstone Bridge scheme. The sensitivity of our scheme permitted us to determine percentage-wise the contents ranging from 0 to 100% helium with an accuracy of up to ± 0.5%, from 0 - 10% helium with an accuracy of up to 0.02%, and from 90 to 100% helium with an accuracy of up to ± 0.05%. Equilibrium curves of the mixture He - N_2 were measured at 68° and 78^oK and under pressures of 10 to 150 atm.

Having obtained sufficient solubility of helium in a liquid phase during static conditions, and 99% pure helium in a gaseous phase, we proceeded to investigate this mixture under dynamic conditions in order to approximate this condition to the condition of working aggregates, at which time the mixture under examination was passed through the column at any predetermined rate. In this instance we worked with two types of columns: (1) A column (Fig. 2) designed to perform up to 30 atm; (2) The so-called separator (Fig. 3) designed to perform up to 200 atm.

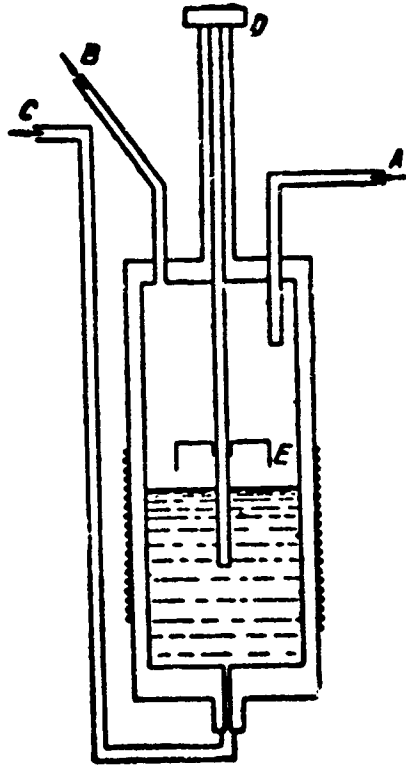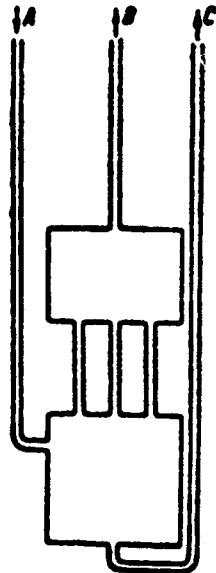By using these two columns we performed a series of tests on
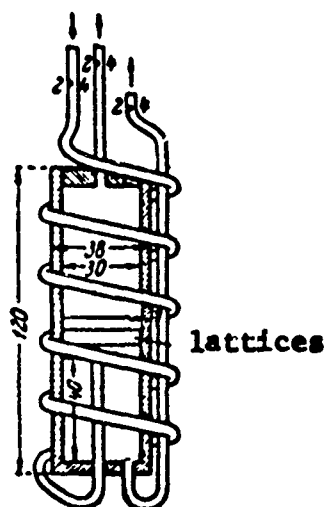
Figure 1.

Figure 2.

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Figure 3.

concentrated mixtures of 0.8, 1, 10, 15, 30, and 60% helium in pressure

ranges from 5 to 150 atm and under 4 different temperatures: 64, 78,

90 and 108° K. The mixture passed from the cylinder through a valve

into the column on the separator, which was immersed in a Dewar vessel

with either liquid nitrogen, oxygen, or methane. The pressure of the

mixture was measured by means of controlled manometers with an accuracy

of up to 0.1 atm, and the rate of both phases was measured by means

of differential manometers. By passage of the mixtures with various

percentages of helium and at various rates from 0.5/min to 3 1/min,

we concluded that the concentration of the mixture was of no influence

on the solubility and purity of helium, and that the passage rate of

the liquid phase was of no noticeable influence on the purity of a

gaseous phase. Table I illustrates the results of a typical test.

It is evident that after an equilibrium is established, the solution

Table I.

Test 10
Composition of the incoming gas 1.1% He. Pressure 30 atm.
Temperature 78° K. Investigation of the gaseous phase.

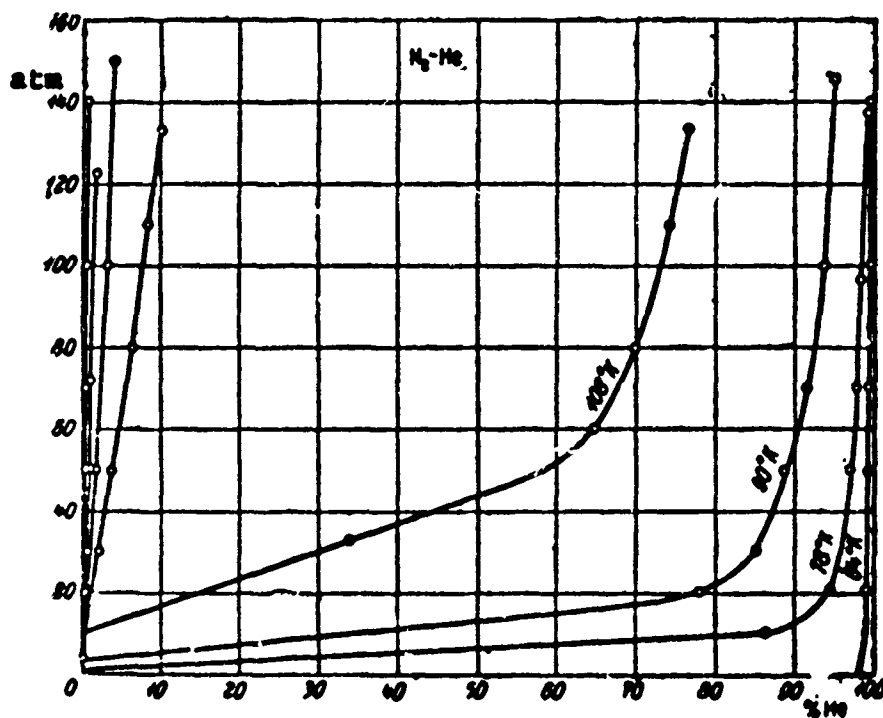| Rate of the liquid phase in lit/min	Percent He					
2	78.5	89	92	95	96.5	96.5
3	96.5	96.5	96.5	**96.5**		
4	91.5	94.0	96.5	96.5	96.5	

Figure 4. p-x diagram, N_2 - He.

remains constant and is not dependent on the rate.

As a result of examining a whole series of equilibrium curves of
the mixture He - N_2 in the above indicated pressure ranges and temperatures,

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we plotted the corresponding diagram (Fig. 4). These clearly indicate that it is possible to obtain helium in a pure state of 99% and higher by not using high pressures, since the purity of helium does not depend on the pressure under low temperatures.

All diagrams may be briefly explained by the following basic traits: (1) The lower the temperature, the higher the concentration of helium in a gaseous phase under all pressures; (2) The lower the temperature, the steeper the liquid branch of the curve; (3) Since the expansion of vapor saturation of pure nitrogen increases with the rise of temperature, each equilibrium curve intersects the liquid branches of all those curves which are related to much lower temperatures.

We can conclude from the above results that it is impossible to obtain pure helium or nitrogen simultaneously under the same temperature by the method of normal condensation, even under high pressures and low temperatures. However, the technical process of separating gases actually occurs, not during constant temperature, but under constant pressures. Therefore, it is possible to study rectification and dephlegmation processes by knowning the diagrams of a binary mixture. We can derive a general view of curves T - x (Fig. 5) from the features of curves p - x. As an example, let us examine a certain pressure p which is lower than the critical pressure of nitrogen. At each point of the ordinate of pure nitrogen in diagram p - x, a pair of curves should originate corresponding to a determined temperature particularly at point A, also under pressure p. This produces a corresponding point α in diagram T - x. Since all curves in diagram p - x ascend from the
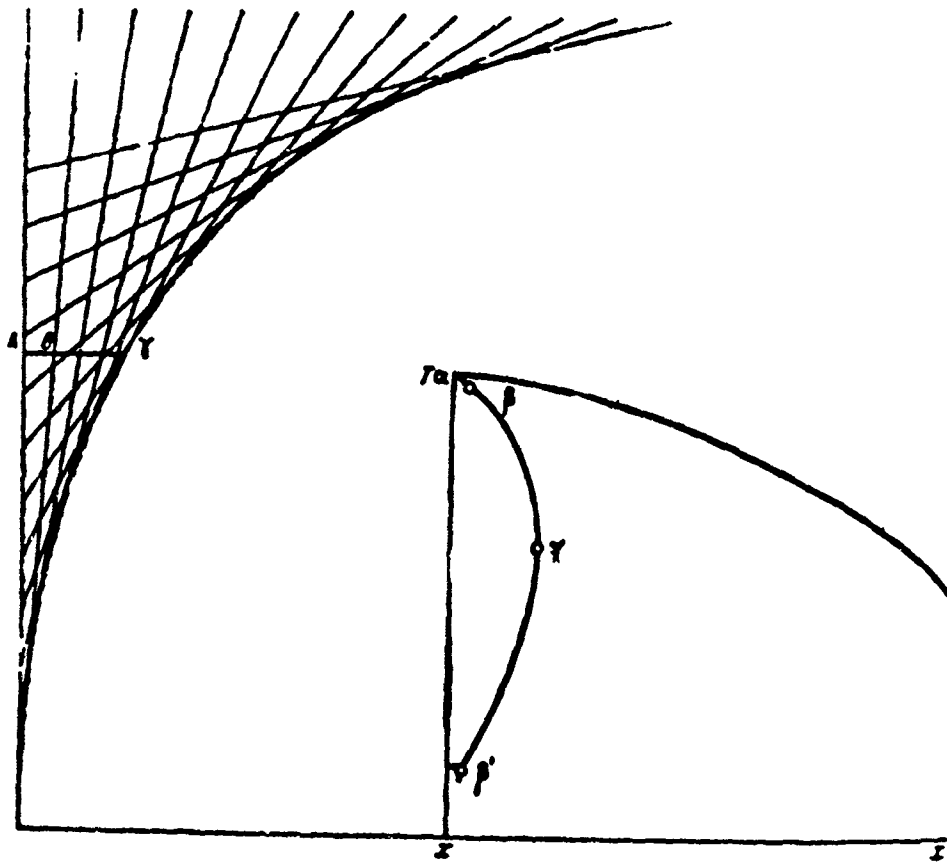
Figure 5.

left to the right side, then the isotherms in the diagram corresponding
to a higher temperature than A do not intersect lines p. Therefore
α is the highest point in diagram T - x for the given pressure. The
isotherm which originates in diagram p - x close to and under A - B,
and which corresponds to a temperature somewhat lower than A, intersects
line p close to A, thereby placing point β slightly lower than α in
diagram T - x. However, the lower the temperature, the closer the
liquid branches are to the axis of nitrogen; therefore, one more liquid
branch will intersect line p at the same point B in diagram p - x and

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will correspond to a lower temperature. This produces point β' in

diagram T - x. The remaining points of the liquid branch in diagram

T - x may now be easily entered. The result will evidently appear

as shown in Figure 5. The shape of the gaseous branch in diagram

T - x follows from the properties (1) of curves p - x. The lower the

temperature, the less helium obtained in a gaseous phase. Two branches

of the highest isotherm originate in point A in diagram p - x. Therefore,

the liquid and the gaseous branches are in concurrence. Both branches

correspond to the isobars encountered at point α as indicated in

Figure 5. The two branches do not extend completely to the bottom

edge of the diagram since, under low temperatures causing a hardening

of nitrogen, new phases emerge which in this case are of no interest

to us. Figure 5 indicates that a point of maximum concentration of

helium in a liquid phase exists. But diagram p - x does not permit

determination of the location of this point. More isotherms, and

particularly more points of lower temperatures, are needed in diagram
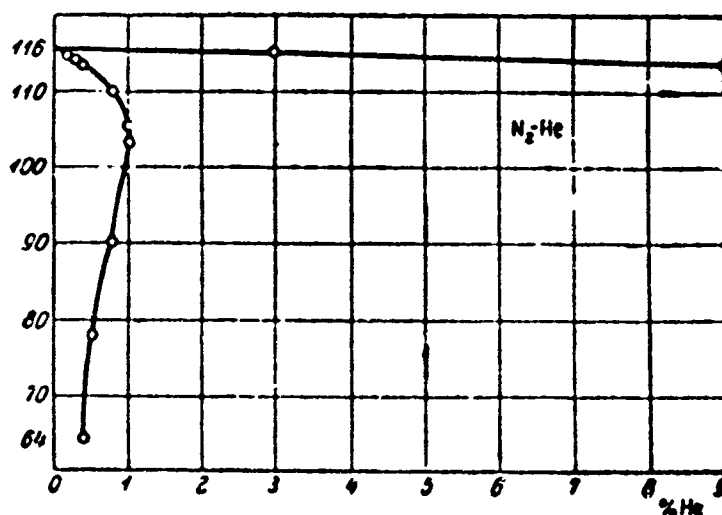
p - x.

Figure 6. T - x - diagram. N_2 - He at 20 atm.

We have completely measured the T - x diagram for separating mixtures
He - N_2 at pressures 4 and 20 atm due to the high values of their
recurviture points. Measurements were performed for low pressures in
a column (Fig. 2). A thermometer indicating vapor expansion was an
additional component of the column, by means of which temperature was
measured with an accuracy of up to $0.1°$. When we measured T - x
diagrams at 20 atm, the thermometer was filled with pure methane; but
when the measurements were performed at 4 atm, it was filled with
oxygen. Working at 20 atm we measured the T - x diagram in a
temperature interval ranging from $116°$ K, the boiling point of pure
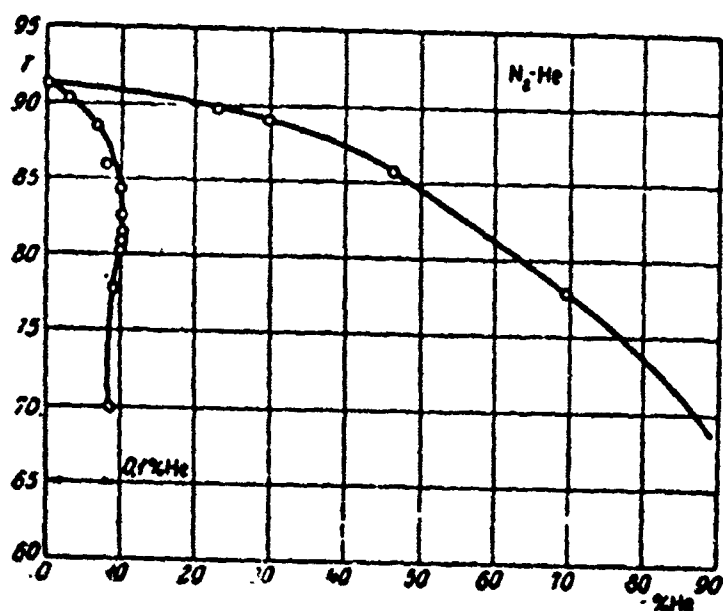nitrogen, to $64°$ K. The curvature point for the liquid phase originated

Figure 7. T - x - diagram. N_2 - He at 4 atm.

in this temperature range. The maximum solubility of helium was
1.0% for this point at 20 atm and at a temperature close to $105°$ K
(Fig. 6). We had to work with various concentrations of helium in

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the mixture in order to obtain all points in the T - x diagram at 20 atm.

A T - x diagram was also measured at 4 atm. In this case we worked in a temperature range of 91° to 70° K and obtained a recurviture point in the range close to 83° K, at which time the maximum solubility of helium equaled 0.11% helium (Fig. 7).
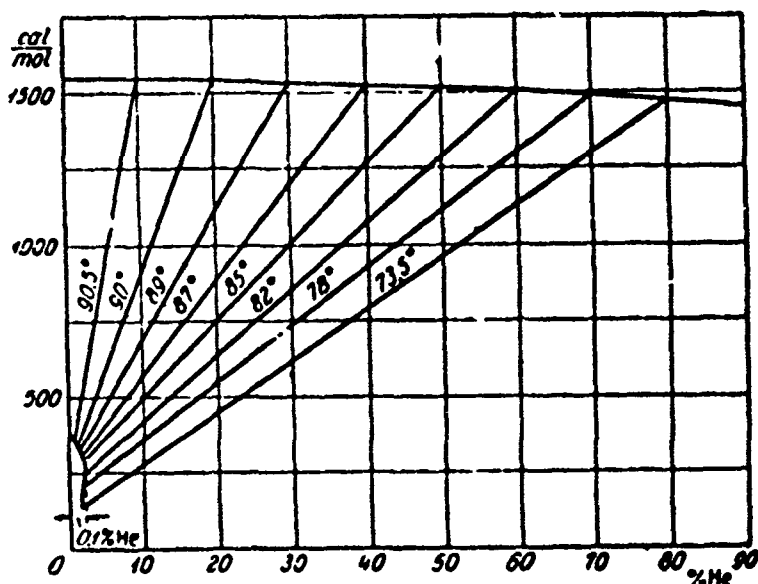

Figure 8. i - x - diagram at 4 atm.

When the problems of dephlegmation and rectification are considered for the purpose of calculating such arrangements, it is beneficial to start with an i - x diagram, which is easily obtained if one knows a T - x diagram of a given mixture as well as an enthropy diagram for nitrogen. Keesom /4/ and Wiseberg /3/ showed how diagram i - x enabled a determination to be made of all data necessary for calculating single and double columns. We plotted diagram i - x at 20 atm for the mixture He - N_2, starting from the above mentioned T - x diagram, and assuming

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that the solubility of helium in liquid nitrogen of up to 1% of

helium does not have a great influence on the thermal evaporation of

nitrogen. On this basis we took λp and i from the enthropy diagram

for N_2. By finding the change of i with the temperature, we plotted

an enthalpy curve for a liquid phase by using a T - x diagram. When

plotting an enthalpy curve for a gaseous phase, we assumed, as Keesom

and Tuyn /5/, that at each concentration the enthalpy value was

additive:

$$i_x = i_{N_2} - \int_{T_{max}}^{116} C_{p_x} dT.$$

By calculating in this manner the precentage for each content of

helium, we obtained a curve for a gaseous phase. This calculation

was initially performed for 1 atm, and we then introduced a correction

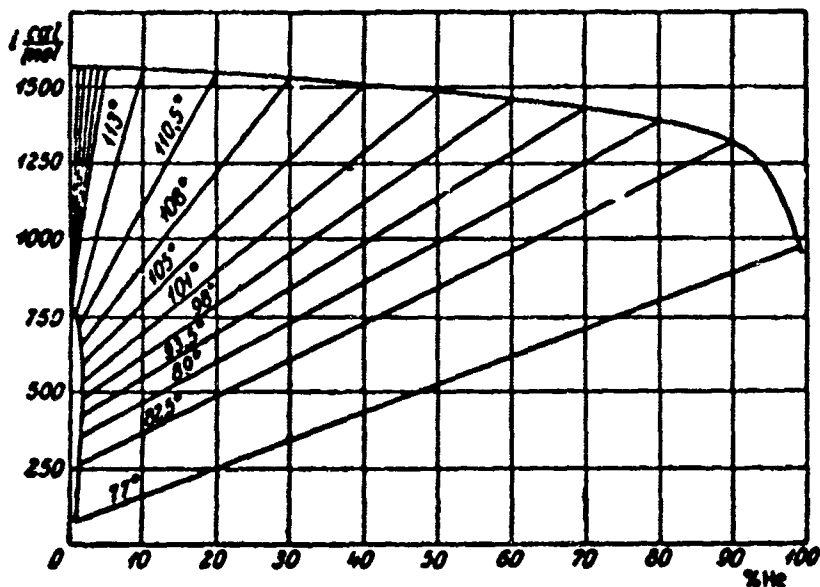on van der Waals forces $\Delta i = \left(B - T\dfrac{dB}{dT}\right)dp.$

Figure 9. i - x - diagram at 20 atm.

The correction was insignificant and hardly changed the curve.

Calculation was also performed under pressures of 4 atm.

Diagrams i - x are shown in Figures 8 and 9. Straight lines connecting equilibrium points on the liquid and the vapor curves are plotted on the diagrams. The temperatures are indicated on these lines.

Having determined p - x, T - x and i - x diagrams, we have set forth all data necessary for calculating any arrangements for separating the mixture He - N_2. Graphic methods of calculating dephlegmators and rectification columns for separating mixtures He - N_2 on the basis of these diagrams are being published simultaneously with this article in the Journal of Chemical Industry.

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