# ON THE LIQUEFACTION OF A MIXTURE OF TWO GASES[1]

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## § 1. Historical

In 1880, L. Cailletet made a very important and entirely unexpected observation. Upon compressing a mixture of one volume of air with five volumes of carbon dioxid, in the apparatus employed by him to liquefy the permanent gases, he observed a portion of the mixture assume the liquid state under a moderate pressure; continuing to increase the pressure gradually, that the temperature might remain constant, he saw the liquid disappear when the pressure had attained a certain value[2]. When the pressure was gradually diminished the liquid reappeared suddenly at the moment of reaching the pressure under which it had disappeared in the first experiment; at any given temperature the meniscus was formed as soon as the pressure had attained a definite value, which was the lower the higher the temperature.

The liquid could thus be distinguished from the gas

| | |
|---|---|
| at 132 atm | at the temperature + 5.5°C |
| 124 | + 10. |
| 120 | + 13. |
| 113 | + 18. |
| 110 | + 19. |

[1] Translated, by J. E. Trevor, from the author's French manuscript.

[2] L. Cailletet. Expériences sur la compression des mélanges gazeux. Comptes rendus **90,** 210 (1880). Jour. de phys. (1) **9,** 192 (1880).

L. Cailletet et P. Hautefeuille. Recherches sur la liquéfaction des mélanges gazeux. Comptes rendus, **92,** 901 (1881).

and finally at 21° the mixture, even when compressed above 390 atmospheres, was no longer liquefied.

Shortly after Cailletet's communication, and without knowledge of it, van der Waals[1] made an analagous observation. In experimenting with a mixture of nine volumes of carbon dioxid with one volume of air he found, at different temperatures, the following values for the pressure $P$ under which the liquid began to appear, and for the pressure $P'$ under which it disappeared :

| | | |
|---|---|---|
| at +29.0°C | $P = 77.5$ atm | $P' = 95$ atm |
| +20.4 | 72 | 103 |
| +19.2 | 72 | 106 |
| + 2.0 | 72 | 149 |

A mixture of seven volumes of carbon dioxid with three volumes of hydrochloric acid gave the following results :

| | | |
|---|---|---|
| at +22.5°C | $P = 69$ atm | $P' = 115$ atm |
| + 0.0 | 39 | 190 |

At the temperature 31.6°C the two pressures became equal at 90 atmospheres.

On the 18th of March, 1886, Stokes communicated to the Royal Society of London a posthumous memoir of Andrews.[2] In this memoir the illustrious physicist studied the compressibility of mixtures of nitrogen and carbon dioxid. Three volumes of carbon dioxid when mixed with four volumes of nitrogen could not be liquefied under any pressure, even at the temperature +2°C. On the other hand a mixture of 6.2 volumes of nitrogen with 1 volume of carbon dioxid exhibited the following behavior : At 3.5°C the liquid began to appear under a pressure of 48.3 atmospheres, the quantity of liquid increasing simultaneously with increase of pressure ; under a pressure of 102 atmospheres the gas was reduced to a small bubble, which finally disappeared. At a higher temperature the phenomenon observed by Cailletet and by van der Waals was

[1] J. D. van der Waals. Die Continuität des gasförmigen und flüssigen Zustandes. Translation by F. Roth, page 143 (Leipzig, 1881).

[2] Andrews. On the Properties of Matter in the Gaseous and Liquid States under Various Conditions of Temperature and Pressure. Phil. Trans. **178**, 57 (1888).

produced ; the liquid after having appeared under a certain pressure disappeared under a greater one.

A mixture of 3.43 volumes of carbon dioxid with 1 volume of nitrogen gave the following values for the pressure $P$ under which the liquid appeared and for the pressure $P'$ under which it disappeared :

| | | |
|---|---|---|
| +6.3°C | $P = 68.7$ atm | $P' = 113.2$ atm |
| 9.9 | 76.6 | 107.8 |
| 13.2 | 91.6 | 103.2 |

It is seen that the values of $P$ and of $P'$ tend to become equal at 98 atmospheres for a temperature of about 14°.

In 1883 Jamin[1] proposed a theory of the curious phenomenon discovered by Cailletet and by van der Waals. Remarking that the critical point of a single fluid is the point where the gas and the vapor have the same density he supposed that at this temperature the liquid does not cease having properties distinct from those of the vapor, but that having the same specific gravity as the vapor it remains mixed therewith, forming with it a fluid apparently homogeneous. Extending this view to the mixture of two fluids, of air and of carbon dioxid for example, he supposed the disappearance of the liquid mixture under a sufficiently high pressure to be only an apparent disappearance ; that the liquid mixture continued to subsist although its density had become equal to that of the gaseous mixture, and that it had diffused into the latter, becoming no longer distinguishable therefrom.

If this theory be true the liquid must disappear under a pressure which is the less the more dense the hardly liquefiable gas which is mixed with the carbon dioxid, and so to make the liquid disappear it would be necessary to employ a much greater pressure when the gaseous component is hydrogen than when it is air ; this result foreseen by Jamin was verified by Cailletet. According to Jamin's explanation of the disappearance of the liquid it would seem that in continuing to compress the system the density of the gaseous mixture should become greater than that of the liquid and that in con-

[1] Jamin. Sur le point critique des gaz liquéfiables. Comptes rendus, **96** (1883); Jour. de phys. (2) **2**, 389 (1883).

sequence the liquid should assemble in the upper part of the tube. Jamin says: «I proposed this second experiment to M. Cailletet, who has made it; the attempt was unsuccessful but I do not yet despair».

The theory of Jamin presents another difficulty not less serious, it is not sufficient that two fluids should have the same density in order that they can form a homogeneous mixture; the experiments of Plateau on the statics of liquids removed from the action of gravity demonstrate this. In order that two fluids initially separated may mix it is necessary that their molecular attractions become the same; at the critical point of a single fluid this condition is evidently satisfied if it be admitted that the liquid and the vapor become identical there; but it is not apparent why two mixtures of carbon dioxid and of air, the one liquid and the other gaseous, should have the same molecular attractions at the moment when they have the same density. Notwithstanding these difficulties of the explanation proposed by Jamin it was still held by Cailletet and Colardeau[1] in 1889.

In 1888 I proposed[2] to abandon Jamin's explanation and to seek to account for the phenomena observed by Cailletet and van der Waals through the theory of double mixtures, as deducible from the principles advanced by J. Willard Gibbs.

Suppose two fluids, 1 and 2, mixed one with the other and forming two layers. The one of these layers is liquid, let it contain a mass $M_1$ of the body 1 and a mass $M_2$ of the body 2; the other layer is gas and may contain a mass $m_1$ of the body 1 and a mass $m_2$ of the body 2.

Let

$$S = \frac{M_2}{M_1}, \qquad s = \frac{m_2}{m_1}, \tag{1}$$

be the concentrations of these two layers. Under the constant pressure $\Pi$ at the temperature $T$ the thermodynamic potential of the first is

[1] Cailletet and Colardeau. Sur l'état de la matière au voisinage du point critique. Ann. chim. phys. (6) **18**, 269 (1889).

[2] P. Duhem. Sur la liquéfaction de l'acide carbonique au présence de l'air. Jour. de phys. (2) **7**, 198 (1888).

$$M_1 F_1(S,\Pi,T)+M_2 F_2(S,\Pi,T),$$

the thermodynamic potential of the second is

$$m_1 f_1(s,\Pi,T)+m_2 f_2(s,\Pi,T),$$

and the system is in equilibrium when

$$\begin{aligned} f_1(s,\Pi,T) &= F_1(S,\Pi,T), \\ f_2(s,\Pi,T) &= F_2(S,\Pi,T). \end{aligned} \qquad (2)$$

If we assign the values of

$$\mathfrak{M}_1 = m_1+M_1,$$
$$\mathfrak{M}_2 = m_2+M_2,$$

the equations (1) and (2) will yield for each pressure $\Pi$ and each temperature $T$ the values of $m_1$, $M_1$, $m_2$, $M_2$.

If we set

$$X=\frac{\mathfrak{M}_2}{\mathfrak{M}_1},$$

we shall obviously find

$$M_1 = G(X,\Pi,T)\mathfrak{M}_1.$$

If $G(X, \Pi, T)$ is positive, this equation will make known the mass $M_1$ of the fluid 1 which is in the liquid state; if $G(X, \Pi, T)$ is negative, the equation constitutes an impossibility and the gaseous mixture will remain homogenous. Between these two general cases appears the particular case where

$$G(X,\Pi,T)=0. \qquad (3)$$

This equation defines, for a gaseous mixture of the concentration $X$ at the temperature $T$, the pressure $\Pi$ under which the mixture will be in equilibrium with an indefinitely small drop of the liquid. Or, if preferred, it defines the *dew point* $T$ of the gaseous mixture having the composition $X$ under the pressure $\Pi$; whence the name of the *dew line* of the mixture of the concentration $X$, given by me in a previous memoir[1] to the line represented by equation (3) when $X$ is regarded as a constant, $T$ as an abscissa and $\Pi$ as an ordinate.

To account for the curious fact demonstrated first by Cailletet

[1] P. Duhem. Dissolutions et mélanges. Troisième Mémoire : Les mélanges doubles. Travaux et mémoires des Facultés de Lille. **3**, No. 13 (1893).

and later by van der Waals it is sufficient to admit that for certain concentrations $X$ of the gaseous mixture the dew line presents two ordinates $\Pi_0$ and $\Pi_1$ for a same abscissa $T$; when compressed at the constant temperature $T$ the gaseous mixture will remain homogeneous under pressures less than $\Pi_0$; under the pressure $\Pi_0$ the liquid will appear, the system will contain gas and liquid together between the pressures $\Pi_0$ and $\Pi_1$; and finally under the pressure $\Pi_1$ the liquid will disappear not to appear again under any pressure. When the temperature $T$ rises towards a certain temperature $\vartheta$ the two pressures $\Pi_0$ and $\Pi_1$ tend towards a common limit $\pi$, in such wise that the dew line has a form similar to that represented by Fig. 1.

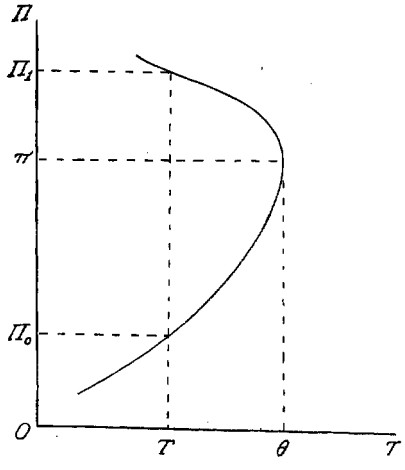


FIG. 1.

My paper was already printed when there appeared in the Philosophical Transactions of the Royal Society of London a posthumous memoir by Andrews[1], which Stokes had presented to this Society on the 18th of March, 1886. In this memoir the illustrious discoverer of the critical point studies the compressibility of a mixture of nitrogen and of carbon dioxid, finding again the phenomenon discovered by Cailletet.

A mixture of 3.43 volumes of carbon dioxid with one volume of nitrogen gave the following values for the pressure $\Pi_0$ under which the liquid appeared and for the pressure $\Pi_1$ under which it disappeared :

| | | |
|---|---|---|
| +0.3°C | $\Pi_0 = 68.7$ atm | $\Pi_1 = 113.2$ atm |
| 9.9 | 76.6 | 107.8 |
| 13.2 | 91.6 | 103.2 |

[1]Andrews. On the properties of matter in the gaseous and liquid states under various conditions of temperature and pressure. Phil. Trans. **178**, 37 (1888).

It is seen that the values $\Pi_0$ and $\Pi_t$ tend to become equal, and equal to 98 atmospheres for a temperature of about $+14°C$, in conformity with the indications of my theoretical ideas.

It results clearly from the formulas given by me in 1888 that, in the system compressed at the constant temperature $T$, the liquid mass passes from zero at the pressure $\Pi_0$ to return to zero when the pressure again assumes the value $\Pi_t$; and that, consequently, in the interval the liquid mass increases, passes through a maximum, and then decreases. These propositions are such obvious consequences of my formulas that I did not think it necessary to state them explicitly. I did not suppose it could be doubted that they result from my view, yet this doubt has been raised, so it must be considered. In the observations of Cailletet, of van der Waals and of Andrews the liquid mass did not approach disappearance by decreasing to zero amount, the surface separating the liquid and the gas became simply plane and indistinct when the pressure approached $\Pi_t$; it then disappeared and the two seemed homogeneous.

In comparing the results of my theory with the observations of the experimenters cited I drew attention only to the general accordance between them, without seriously considering this partial lack of agreement, for it did not seem to me at all improbable that Cailletet, van der Waals and Andrews had not really observed states of equilibrium. In these phenomena, as in the vaporization of a liquid near its critical point, the *viscosity*, negligible under other circumstances, assumes a considerable importance; the equilibrium is established with an extraordinary slowness, from which must follow apparent contradictions between the results of rapidly made experiments and the consequences of a theory treating only systems in equilibrium.

P. Kuenen[1] has concluded from my failure to draw attention to this divergence in my memoir of 1888 that I did not at that time admit the existence, between the pressures $\Pi_0$ and $\Pi_t$, of a progressive condensation causing the mass of the liquid to increase continuously from zero *and followed by a retrograde condensation decreas-*

[1]Kuenen. On the condensation of a mixture of two gases. Communications from the laboratory of physics at the University of Leiden. No. 13 (1894).

*ing this mass continuously to zero.* To sustain this opinion would be to maintain that I did not understand the formulas which I advanced nor the reasoning through which they were established. Kuenen could argue from my silence concerning this apparent experimental contradiction to accuse me of temerity ; but he himself has brought me justification, for in taking care to agitate the gaseous mixtures studied, in order to assure the prompt establishment of states of equilibrium, he has observed[1] the appearance of the retrograde condensation which stood already written in my formulas.

The object of Kuenen's first paper was to supply experimental data for an important theory developed by van der Waals[2]. If the concentration of the mixture be denoted by $s$, its density by $\rho$, and its absolute temperature by $T$, the inner themodynamic potential of its unit of mass can be represented by $Z(\rho, s, T)$. It has two different values, depending upon whether the mixture is in the liquid state or in that of gas ; van der Waals admits that these two values are two different determinations of the same multiform analytic function. He then introduces the following change of variables :

$$\rho = \frac{1}{v}, \qquad s = \frac{x}{1-x},$$

which transforms the function $Z(\rho, s, T)$ into a function $\psi(x, v, T)$. Leaving then the temperature $T$ constant and representing in three rectangular axes the values of the variables $x$, $v$ and $\psi$, he proposes to construct the surface

$$\psi = \psi(x, v, T).$$

With this surface constructed, the properties of the mixture, its homogeneous constitution or its separation into two layers, can be studied by the methods which Gibbs has applied to the surface representing the inner thermodynamic potential of a single fluid as a function of its specific volume and of its temperature.

In order to determine the form of the surface $\psi$, van der Waals is obliged to introduce numerous hypotheses. In the first place he

[1] Kuenen. Mésures concernant la surface de van der Waals pour des mélanges d'acide carbonique et de chlorure de methyle. Arch. néerl. **26**, 394 (1892).

[2] van der Waals. Théorie moléculaire d'une substance composée de deux matières différentes. Ibid, **24**, 1 (1891).

supposes that the specific volume $v$, the pressure $\Pi$ and the temperature $T$ are united through a relation of the form

$$\Pi = \frac{RT}{v-b} - \frac{a}{v^2},$$

previously proposed by him for a single fluid; but here $a$ and $b$, instead of being constants, are functions of $x$, he assigns to them expressions of the following form:

$$\begin{cases} a = a_1(1-x)^2 + 2a_{12}x(1-x) + a_2x^2, \\ b = b_1(1-x)^2 + 2b_{12}x(1-x) + b_2x^2, \end{cases} \qquad (4)$$

where $a_1$, $a_{12}$, $a_2$, $b_1$, $b_{12}$, $b_2$ are six constants.

The expression of $\Pi$ as a function of $v$, $x$ and $T$ can serve through aid of the well known equation

$$\frac{\partial}{\partial v}\psi(x,v,T) + \Pi = 0,$$

for the determination of $\psi(x, v, T)$, nevertheless it determines this function $\psi(x, v, T)$ only *with a function of the variables x and T left arbitrary*. Through a series of considerations, whose precision leaves something to be desired, van der Waals succeeds in *suppressing this function*, whereby $\psi$ is reduced to the form

$$\psi = -\log(v-b) - \frac{a}{v} + RT[x\log x + (1-x)\log(1-x)] \qquad (5)$$

where $a$ and $b$ have the values (4). He admits finally that one must have, for the stability of the mixture, the inequality

$$\frac{\partial^2\psi}{\partial x^2}\frac{\partial^2\psi}{\partial v^2} - \left(\frac{\partial^2\psi}{\partial x \partial v}\right)^2 > 0$$

but this inequality, taken from Gibbs, has not been established in a satisfactory manner, as I have elsewhere remarked[1].

Notwithstanding the employment of all these hypotheses van der Waals cannot *deduce* from the equation of the surface $\psi$ the necessity of the curious phenomenon observed by Cailletet and himself[2], he shows only that it is possible to conceive a mode of variation

[1] P. Duhem. Dissolutions et mélanges. Premier Mémoire: Equilibres et mouvement des fluides mélangés. Travaux et Mémoires des Facultés de Lille. No. 11, 90 (1892).

[2] van der Waals. *l. c.* 54.

of this surface with the temperature which accords with that observation ; in the paper of van der Waals, therefore, as in that published by me three years before, the retrograde condensation is regarded not as a consequence of the theory but as a result which the theory must be made to represent.

The University of Leyden having set for competition the following question : « Required observations serving to check the theory of van der Waals concerning mixtures of two substances », Kuenen presented a paper which was awarded the prize[1]. In this work Kuenen analyzes the mode of variation of the fold devised by van der Waals to make the general form of the surface $\psi$ conform with the phenomenon of retrograde condensation. He shows that the form of the dew curve must be that represented by Fig. 2. This curve rises from left to right to the point $M(\Theta,\pi)$ ; it then rises further, from right to left, up to the point $Z(\Theta,\mathfrak{P})$ where it terminates. At temperatures above $\Theta$ no condensation is possible ; at temperatures below $\Theta$ only normal condensation can appear, and finally, at temperatures between $\Theta$ and $\Theta$ a normal condensation followed by retrograde condensation is observed.

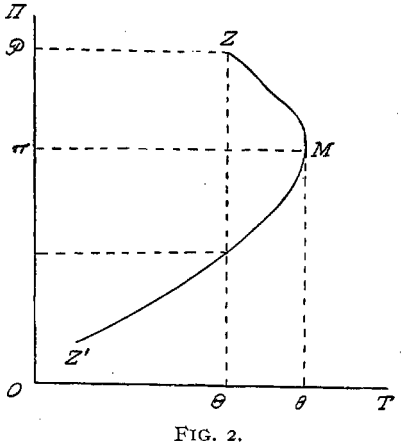

FIG. 2.

The point $M(\Theta,\pi)$, which had already figured in my exposition, received from Kuenen the name of *point of critical contact ;* the point $Z(\Theta,\mathfrak{P})$, which I had not considered at all, is called the *point of folding*. These terms are chosen because of the parts played by these points in the surface of van der Waals. Kuenen made definite

[1]P. Kuenen. Metingen betreffende het opperolak van van der Waals voor mengsels van Koolzuur en chlormethyl. Proefschrift. Leiden (1892). Measurements relating to the surface of van der Waals for mixtures of carbonic acid and methyl chloride. Arch. néerl. **26** (1892).

the idea of the point of folding by remarking[1] that *in this point the liquid mixture and the gaseous mixture become identical.*

One is led in fact, by generalization of the theories relative to the continuity of the liquid and gaseous states, to conclude that the two functions $f_1(s, \Pi, T)$ and $F_1(s, \Pi, T)$ are two branches of the same multiform analytic function ; and that this is also true of the functions $f_2(s, \Pi, T)$ and $F_2(s, \Pi, T)$. In every point $(\mathfrak{S}, \mathfrak{P}, \Theta)$ of a given *critical line*, the two functions $f_1$ and $F_1$ unite and are then prolonged in a single function ; the two functions $f_2$ and $F_2$ unite likewise to be prolonged in a single analytic function. In the $(T, \Pi)$-plane the critical line of the space is projected as a plane critical line uniting the critical point $C_1$ of the pure fluid 1, $(s=0)$, with the critical point $C_2$ of the pure fluid 2, $(s=\infty)$. I developed[2] in 1893 this notion of the critical line and proposed, as a consequence, to give the name *critical point*, of the gaseous mixture of the composition $X$, to the point $Z(\mathfrak{P}, \Theta)$ where the dew curve of this mixture terminates,—to the point termed by Kuenen the *point of folding*.

How, now, does the dew line vary when the concentration $X$ of the gaseous mixture varies from zero to infinity? I have supposed that, for every concentration $X_1$, $X_2$, sufficiently near zero or infinity, the dew curve rises continuously from left to right as do the curves $X_1X'_1$, $X_2X'_2$, of the figure 3 ; for such a concentration the retrograde condensation could not appear. This phenomenon would appear only for the concentrations $Z$ comprised between a lower limit $Y_1$ and an upper limit $Y_2$ ; to such a concentration would correspond a dew curve like $ZZ'$. To the two limiting concentrations $Y_1$ and $Y_2$ there would

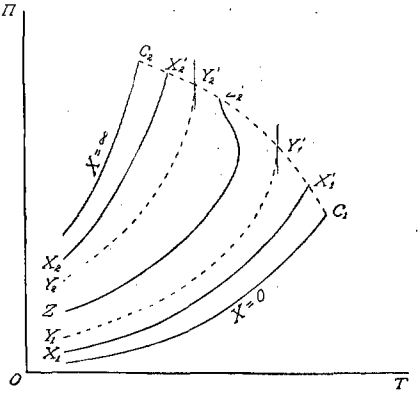


FIG. 3.

[1] Kuenen. *l. c.* No. 42.

[2] P. Duhem. Dissolutions et mélanges. Troisième Mémoire : Les mélanges doubles. Chap. 2 and 3. Travaux et Mémoires des Facultés de Lille. No. 13.

correspond dew curves $Y_1Y'_1$, $Y_2Y'_2$, which would cut the critical line in points $Y'_1$, $Y'_2$ where they would have vertical tangents.

Kuenen[1] has shown that this shape of the dew curves is not in conformity with the geometric theory of van der Waals; that whatever the composition $X$ of the gaseous mixture, the dew curve has the shape which is assigned in Fig. 3 to the line $ZZ'$, such that for every composition of this mixture the retrograde condensation is observable. He has sought to demonstrate, further, that this view follows from the principles posited by me; to supply this demonstration he has proceeded much as follows:—

He remarks very justly at the outset that to the *dew curve* of the *gaseous* mixture having the concentration $X$—*i. e.*, the curve indicating at each temperature $T$ the pressure $\Pi$ under which the mixture ceases to be homogeneous or commences to be so—one must join the *boiling curve* of the *liquid* mixture of the concentration $X$, *i. e.*, the curve which indicates under what pressure $\Pi$ at each temperature $T$ the liquid homogeneous mixture of the concentration $X$ can be in equilibrium with an indefinitely small gaseous bubble.

The equation of the boiling line is then obtained by the procedure which yields the equation of the dew line; it suffices to permute the functions $f_1$ and $F_1$ as well as the functions $f_2$ and $F_2$. If it be recollected that the functions $f_1$ and $F_1$ are but two distinct determinations of two multiform analytic functions, and that the same is true of the two functions $f_2$ and $F_2$, it is seen that the dew line of a gaseous mixture having the concentration $X$ and the boiling line of a liquid mixture of the same concentration $X$ are but two different branches of the same curve, and it is seen further that these two branches must meet at the same point of the critical line $C_1C_2$. Kuenen has succeeded in deducing from my formulas that the dew line and the boiling line must have the same tangent at this critical point.

*Do these two lines meet at the critical point so as to form a single analytic line, or are they mutually tangent in such wise as together to form a curve whose critical point is a cusp?* Both hypotheses are admissible.

[1] Kuenen. On the Condensation of a Mixture of two Gases. Communications from the Laboratory of Physics at the University of Leiden. No. **13** (1894).

Of these two hypotheses Kuenen adopts the first. The critical line $C_1C_2$ is then, as can easily be shown, tangent to the two lines, the dew curve and the boiling curve, at the point where the latter meet. The dew line $XY$ and the boiling line $ZY$ form thus a curve as represented by Fig. 4.

In the region $XYC_1$, the mixture in equilibrium is in the state of homogeneous vapor, in the region situated beyond the critical line $C_1C_2$ it is in the state of homogeneous gas, in the region $C_2YZ$ it is in the state of homogeneous liquid, and in the region $XYZ$, finally, it is partly in the state of vapor, partly in that of liquid.

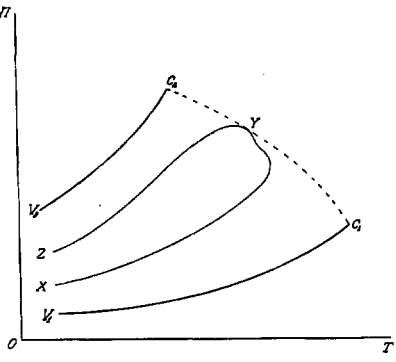


FIG. 4.

When the concentration $X$ tends toward zero or towards infinity the two branches of the curve, $XY$, $ZY$, tend towards each other in such wise as to approach either the curve $V_1C_1$ of the vapor pressures of the liquid 1, or the curve $V_2C_2$ of the vapor pressures of the liquid 2 ; each of these curves must be considered in the actual problem as a *double line*, playing at the same time the parts of dew line and of boiling line. One of the two lines, $ZY$, $XY$, must, in a part of its extent, be met twice by a same ordinate ; Kuenen admits that this property belongs always to the line $XY$, now if this were true *the phenomenon of retrograde condensation could be observed for every concentration of the gaseous mixture between zero and infinity*.

This conclusion of Kuenen is seen to rest upon two assumptions which are not above objection, for the recent experiments made by this physicist[1] on the liquefaction of mixtures of ethane and of peroxid of nitrogen relate to a case where the dew line and the boiling line lie too close together for it to be possible to draw from the exper-

[1]Kuenen. On the Condensation and the Critical Phenomena of Mixtures of Ethane and Nitrous Oxide. Communications from the Laboratory of Physics of the University of Leiden. No. **16** (1895). Phil. Mag. [5] **40**, 173 (1895).

iments any very positive conclusion either for or against the existence of a cusp at the junction of the two. Now, if the dew line and the boiling line do meet to form a cusp, my hypothesis concerning the form of the dew lines would be perfectly admissible.

It has therefore seemed to me to be worth while to investigate whether the general theorems which I have established concerning double mixtures will not furnish a means of elucidating the contested points of this problem; the results which I have reached, and which are set forth in the present paper, confirm Kuenen's view—much to my gratification.

## § 2. Condensation and Retrograde Condensation

Let us consider the critical line of a mixture of two bodies 1 and 2; this line connects the critical point $C_1(\mathfrak{P}_1, \Theta_1)$ of the fluid 1 with the critical point $C_2(\mathfrak{P}_2, \Theta_2)$ of the fluid 2.

*We shall suppose, in the first place, that, whatever be the concentration of the mixture, its critical pressure will lie between the critical pressures, $\mathfrak{P}_1$ and $\mathfrak{P}_2$ of the fluids 1 and 2.*

There is nothing necessary in this hypothesis, but it holds good in every case which has been experimentally studied. If a mixture should be found whose behavior does not accord with it, the following reasoning must, for that mixture, be replaced by analogous but more complicated expressions.

We shall not make an analogous hypothesis concerning the critical temperatures of mixtures, experiment in fact, supplies mixtures whose critical temperatures lie below the critical temperatures of the component fluids; such is, according to Dewar[1], a mixture of $CO_2$ and $C_2H_2$ and, according to Kuenen[2], a mixture of $NO_2$ and $C_2H_6$.

The hypothesis just formulated is contained, at least in so far as all particular consequences are concerned, in the following hypothesis, which likewise is true for all mixtures yet experimentally studied, and which is taken as the point of departure of the reasoning to be adduced:

*There exists one and only one mixture of the two fluids 1 and 2*

[1]Proc. Roy. Soc. **30**, 543.

[2]Communications from the Laboratory of Leiden. No. **16**, page 21.

*having for its critical pressure a certain pressure* $\mathfrak{P}$ *lying between* $\mathfrak{P}_1$ *and* $\mathfrak{P}_2$.

We designate the concentration of this mixture by $\mathfrak{X}(\mathfrak{P})$ and its critical temperature by $\Theta(\mathfrak{P})$; $\mathfrak{X}(\mathfrak{P})$ and $\Theta(\mathfrak{P})$ are, according to the foregoing hypothesis, uniform functions of $\mathfrak{P}$.

There exists an analytic function, continuous but multiform, of the three variables $x, \Pi, T$,—say $\psi_1(x, \Pi, T)$—which coincides, according to the case, either with the function $f_1(x, \Pi, T)$ or with the function $F_1(x, \Pi, T)$. Let us select a constant pressure $\mathfrak{P}$, lying between $\mathfrak{P}_1$ and $\mathfrak{P}_2$, and examine the manner in which the function $\psi_1(x, \mathfrak{P}, T)$ varies with the concentration $x$ and the temperature $T$.

At temperatures $T$ above $\Theta(\mathfrak{P})$, the mixture of the concentration $x$ is homogeneous, whatever value $x$ may have; if the pressure $\mathfrak{P}$ and the temperature $T$ are maintained constant, the function $y = \psi_1(x, \mathfrak{P}, T)$ is a constantly and continuously decreasing function of $x$, represented, from $x = 0$ to $x = +\infty$, by an analytic curve such as $\Phi_1\varphi_1$ (Fig. 5).

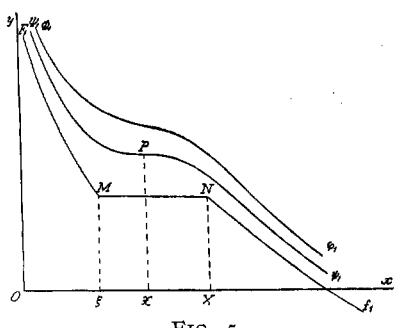

FIG. 5.

At temperatures below $\Theta(\mathfrak{P})$ it can happen that the mixture having the gross concentration $x$ separates into two layers, the one liquid the other gaseous, of different concentrations; for an assigned value $T$ of the temperature, the pressure $\mathfrak{P}$ remaining fixed, the concentration $\xi$ of the liquid layer and the concentration $X$ of the gaseous layer have determinate values.

In certain cases the two preceding propositions must be replaced by those obtained through interchanging the words: *temperatures above* $\Theta(\mathfrak{P})$, *and temperatures below* $\Theta(\mathfrak{P})$. We shall commence by studying the case just defined, which shall be termed the First Case; we shall then pass to the inverse or Second Case.

Suppose, to fix our ideas, that

$$\mathfrak{P}_2 > \mathfrak{P}_1$$

we admit then that continually

$$X > \xi.$$

When $X$ varies from o to $\xi$, the function $\psi_1(x, \mathfrak{P}, T)$ coincides with the function $F_1(x, \mathfrak{P}, T)$; when $x$ varies from $X$ to $+\infty$, the function $\psi_1(x, \mathfrak{P}, T)$ coincides with the function $f_1(x, \mathfrak{P}, T)$. If it be observed that

$$f_1(X, \mathfrak{P}, T) = F_1(\xi, \mathfrak{P}, T),$$

it is seen that the first branch of the function is represented by the descending curve $F_1 M$ (Fig. 5) and that its second branch is represented by the descending curve $Nf_1$, the two points $M$, with the abscissa $\xi_1$ and $N$ with the abscissa $X$, have the same ordinate.

Finally, if the temperature $T$ is equal to $\Theta(\mathfrak{P})$, the curve represented by the equation

$$y = \psi_1(x, \mathfrak{P}, \Theta)$$

is a curve $\Psi_1\psi_1$ (Fig. 5), which falls continuously from left to right, save at the point $P$, with the abscissa $\mathfrak{X}(\mathfrak{P})$, where it presents a point of inflection with a horizontal tangent.

Thus, *under the given pressure* $\mathfrak{P}$, at each temperature $T$, there is an entirely determinate curve

$$y = \Psi_1(x, \mathfrak{P}, T),$$

which may be termed the Isotherm relative to the temperature $T$.

If for the curve

$$y = \Psi_2(x, \mathfrak{P}, T),$$

there be substituted that represented by the equation

$$y = \Psi_1(x, \mathfrak{P}, T) + G(T),$$

where $G(T)$ is an arbitrary function of the temperature $T$, there is obtained a new curve which is deduced from the first by displacement of all its points, in the direction parallel to $Oy$, through the same distance $G(T)$. One can evidently make disposition of the function $G(T)$ in such manner that the isotherms which correspond to any two different temperatures may have no common point at a finite distance, and that to the temperatures $T, T', T''$, . . . all lying below $\Theta(\mathfrak{P})$ and arranged in order of increasing magnitude, there correspond straight lines $MN, M'N', M''N''$, . . . whose ordinates are also arranged in the order of increasing magnitude (Fig. 6). Such a disposition greatly facilitates the discussion, it shall be supposed in the following to be always realized.

The curve which is the locus of the points $M, M', M''$, . . . and that which is the locus of the points $N, N', N''$, . . . terminate at the point $P$; from analogy with the teachings of the theory of the continuity of the liquid and gaseous states, regarding the isotherms of a single fluid, we are led to admit the following hypothesis—upon which this entire discussion rests:

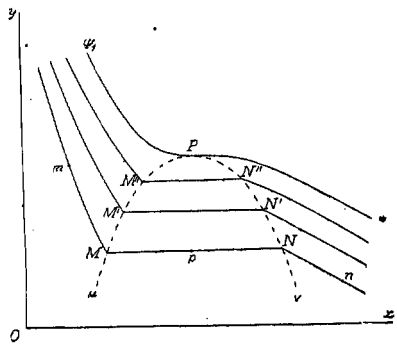

FIG. 6.

HYPOTHESIS.—*The curve which is the locus of the points* $M, M', M''$, . . . *and that which is the locus of the points* $N, N', N''$, . . . *have in* $P$ *a common tangent parallel to* $Ox$,—*they extend each other.*

The line $\mu P \nu$ formed by these two curves (Fig. 6) possesses remarkable properties.

1st. Take a point $m$, whose abscissa is $x$, *in the region* $\Psi_1 P\mu$. Through this point there passes a line

$$y = \Psi_1(x, \mathfrak{P}, T),$$

corresponding to a certain temperature $T$; *under the pressure* $\mathfrak{P}$, *at the temperature* $T$, *the mixture having the total concentration* $x$ *is in the homogeneous liquid state.*

2d. Take a point $n$, whose abscissa is $x$, *in the region* $\nu P \psi_1$. Through this point there passes a line

$$y = \psi_1(x, \mathfrak{P}, T),$$

corresponding to a certain temperature $T$; *under the pressure* $\mathfrak{P}$, *at the temperature* $T$, *the mixture with the total concentration* $x$ *is in the homogeneous gaseous state.*

3d. Take finally a point $p$, whose abscissa is $x$, *in the interior region of the curve* $\mu P \nu$. Through this point draw a parallel to $Ox$; this line will meet the curve $\mu P \nu$ in two points $M$, $N$, where terminate two branches of the same curve

$$y = \psi_1(x, \mathfrak{P}, T),$$

corresponding to a certain temperature $T$. This curve corresponds

to a certain temperature $T$. *Under the pressure* $\mathfrak{P}$, *at the temperature* $T$, *the mixture of the total concentration* $x$ *is partly in the liquid state and partly in that of vapor.*

The foregoing propositions can be enunciated briefly in the statement that, *under the pressure* $\mathfrak{P}$,

1st. *Every point of the region* $\Psi_1 P\mu$ *represents a homogeneous liquid state;*

2d. *Every point of the region* $\Psi_1 P\nu$ *represents a state of homogeneous vapor;*

3d. *Every point of the region* $\mu P\nu$ *represents a heterogeneous state.*

Let us consider the part of the curve $\mu P\nu$ (Fig. 7) in the neighborhood of the point $P$, whose abscissa is $\mathfrak{X}(\mathfrak{P})$.

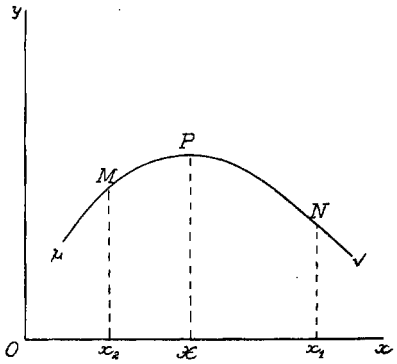

FIG. 7.

We will take a value $x_1$ of $x$, in the neighborhood of $\mathfrak{X}(\mathfrak{P})$ and above it, from the abscissa $x_1$ we will draw a parallel to $Oy$; this parallel meets the curve $\mu P\nu$ at a point $N$, which belongs to the isotherm for a certain temperature $T_1$, lower than $\Theta(\mathfrak{P})$. According to the preceding theorems, $T_1 < \Theta(\mathfrak{P})$ and $\mathfrak{P}$ will be the abscissa and the ordinate of a point of the dew line of the mixture having the concentration $x_1 > \mathfrak{X}(\mathfrak{P})$. Further, if we set

$$\mathfrak{X}P = Y, \qquad x_1 N = y_1,$$

the ratio

$$\frac{Y - y_1}{\mathfrak{X} - x_1}$$

will be indefinitely small. But it is clear that $(Y - y_1)$ is, in general, of the same order of magnitude as $[\Theta(\mathfrak{P}) - T_1]$, in such wise that the ratio

$$\frac{\Theta(\mathfrak{P}) - T_1}{\mathfrak{X}(\mathfrak{P}) - x_1}$$

will be indefinitely small.

We will take, next, a value $x_2$ of $x$, near to $\mathfrak{X}(\mathfrak{T})$, and less than $\mathfrak{X}(\mathfrak{T})$; at the abscissa $x_2$ we will draw a parallel to $Oy$; this parallel meets the curve $\mu P v$ in a point $M$ belonging to the isotherm for a certain temperature $T_2$ lower than $\Theta(\mathfrak{T})$. According to the preceding theorems, $T_2 < \Theta(\mathfrak{T})$ and $\mathfrak{T}$ will be the abscissa and ordinate of a point of the boiling line of the mixture having the concentration $x_2 < \mathfrak{X}(\mathfrak{T})$. One readily sees, further, that the ratio

$$\frac{\Theta(\mathfrak{T})-T_2}{\mathfrak{X}(\mathfrak{T})-x_2}$$

is indefinitely small. It will be seen that these theorems involve the correctness of the propositions under discussion.

Let us take (Fig. 8) the temperature axis as axis of abscissas and the pressure axis as that of ordinates; let $C(\Theta,\mathfrak{T})$ be a point of the critical line, corresponding to the value $\mathfrak{X}$ of the concentration. From the point $C$, we will draw a parallel $\mathfrak{T}C$ to the temperature axis. That part of this line $\mathfrak{T}C$ lying beyond the point $C$ meets, in the neighborhood of the point $C$, neither the dew line nor the boiling line for a mixture whose concentration lies near $\mathfrak{X}$. On the contrary, from every point $M$, near to the point $C$ on the line $\mathfrak{T}C$ and lying to the left of the point $C$, there passes a dew line for a mixture of the concentration $x_1$, greater than $\mathfrak{X}$ and very near it; and a boiling line for a mixture $\mathfrak{X}$ of the concentration $x_2$, less than $\mathfrak{X}$ and very near it; furthermore the two ratios

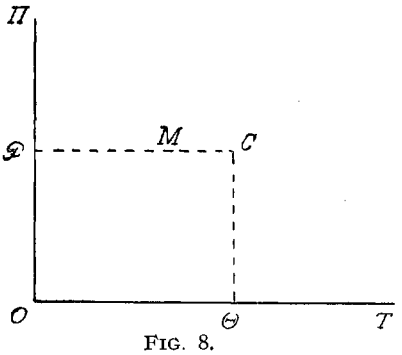

FIG. 8.

$$\frac{\overline{MC}}{x_1-\mathfrak{X}}, \qquad \frac{\overline{MC}}{x_2-\mathfrak{X}},$$

tend towards zero when the point $M$ tends towards the point $C$.

Without further extending this demonstration it may be remarked that to every value $\mathfrak{X}$ of the concentration there corresponds one and but one point $C$ of the critical line, and the reverse;

when $\mathfrak{X}$ varies continuously from zero to unity the point $C$ traverses the critical line from the point $C_1$, the critical point of the pure fluid 1, to the point $C_2$, the critical point of the pure fluid 2. If $C, C'$, be two points lying near the critical line, corresponding to the values $\mathfrak{X}, \mathfrak{X}'$, of the concentration; the ratio $\frac{\mathfrak{X}'-\mathfrak{X}}{\overline{CC'}}$ will tend, in general, towards a finite limit when the two points $C, C'$ tend to come together.

On the other hand we have supposed that

$$\mathfrak{P}_2 > \mathfrak{P}_1$$

and also that there exists one and but one mixture having for its critical pressure some pressure $\mathfrak{P}$ lying between $\mathfrak{P}_1$ and $\mathfrak{P}_2$; it results from this, as is readily seen, that if the concentration of the mixture rises continuously from zero to one, the critical pressure increases continuously from $\mathfrak{P}_1$ to $\mathfrak{P}_2$.

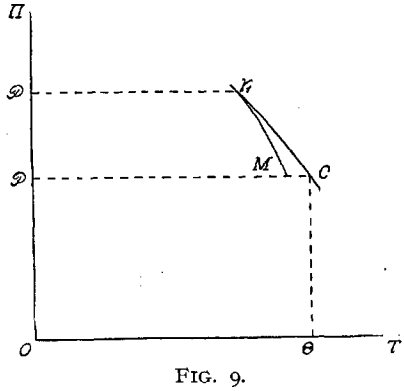

FIG. 9.

These preliminaries settled let us consider a pressure $\mathfrak{P}$ lying between $\mathfrak{P}_1$ and $\mathfrak{P}_2$; the constant ordinate $\mathfrak{P}$ parallel to $OT$ (Fig. 9) meets the critical line in one and but one point $C$, which is the critical point of a mixture having the concentration $\mathfrak{X}$.

Let us take a point $M$ indefinitely near the point $C$ and lying to the right of it. Through this point passes the dew line of the mixture with the concentration $x_1$, indefinitely near to $\mathfrak{X}_1$, and greater than $\mathfrak{X}$.

After what has just been shown, the mixture with the concentration $x_1$ will have as critical point a point $\gamma_1$, with an ordinate $\mathfrak{P}_1$ greater than $\mathfrak{P}$. The line $\gamma_1 C$ will be an element of the critical line, and the line $\gamma_1 M$ an element of the dew line, of the mixture having a concentration $x_1$.

The ratio $\frac{\overline{MC}}{x_1-\mathfrak{X}}$ is infinitesimal; and, on the other hand, it has

been shown that the ratio $\frac{x_1 - \mathfrak{X}}{\gamma_1 C}$ is finite ; but the ratio $\frac{\overline{MC}}{\gamma_1 C}$ is then infinitesimal. Therefore *the dew line MC of the mixture having a concentration $x_1$ is tangent to the critical line $\gamma C_1$ at the critical point $\gamma_1$ of this mixture ; and, furthermore, the dew line falls as it sets out from its point of contact with the critical line.* Since $\mathfrak{X}$ is any concentration whatever, and since the same is true of the concentration $x_1$, which lies indefinitely near it, the preceding theorem is general. It may be demonstrated in an analogous manner *that the dew line of any mixture whatever is tangent to the critical line at the critical point of this mixture, and that the dew line rises as it leaves this point.*

These theorems involve the correctness of the propositions advanced by Kuenen, the dew line and the boiling line of a mixture with an assigned concentration meet at and continue together from the point where they touch the critical line.

At temperatures far from the critical temperature the dew line and the boiling line both rise from left to right, and the boiling line of the mixture having a given concentration lies above the dew line of this mixture ; one must conclude that together they form in general a line having the aspect represented in Fig. 10.

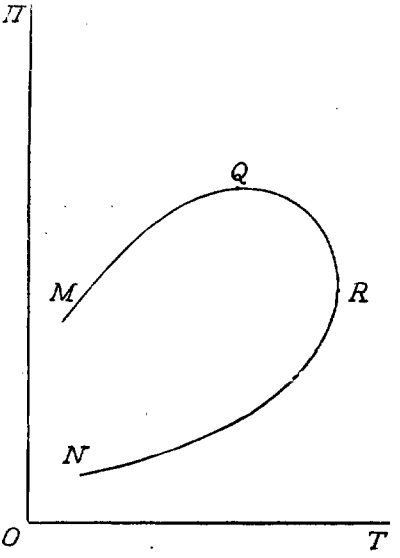


FIG. 10.

This line can have at $Q$ a tangent parallel to the axis $OT$, and at $R$ a tangent parallel to the axis $OP$. The critical point $C$ can not lie upon the branch of the curve $MQ$, for, in setting out from this point, the dew line rises and the boiling line falls, which is contrary to what has just been demonstrated ; only two cases therefore can appear : either the critical point lies between the points $Q$ and $R$, or it lies upon the branch $NR$.

**A.**—*The critical point C lies between the points Q and R* (Fig. 11).

Let us suppose that the *mixture be compressed at constant temperature. If the temperature is lower than the critical temperature* $\Theta$, the mixture is at first entirely in the gaseous state; when the pressure becomes equal to the ordinate of the dew line, the first drop of liquid appears; that portion of the mixture which is in the liquid state increases with the pressure; when the pressure becomes equal to the ordinate of the boiling line the mixture is entirely in the liquid state; it then remains homogeneous however great the pressure may become.

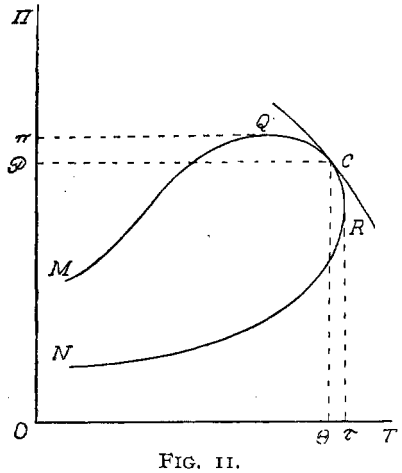

FIG. 11.

If the temperature lies between the *critical temperature* $\Theta$ and the abscissa $\tau$ of the point R, the mixture is at first in the state of a homogeneous gas; when the pressure becomes equal to the first ordinate of the dew line the first drop of liquid appears; that fraction of the mixture which is in the liquid state is at first an increasing function of the pressure; it then passes through a maximum and becomes a decreasing function of the pressure; when the pressure becomes equal to the second ordinate of the dew curve, the last drop of liquid disappears; the mixture remains then in the state of homogeneous gas however great the pressure may become. This is the experimental result of Cailletet.

*If the temperature is greater than the abscissa* $\tau$ *of the point R the mixture will remain homogeneous under all pressures.*

Let us now suppose *that the mixture be taken in a homogeneous liquid state and that it be heated under constant pressure.*

*If the pressure is less than the critical pressure* $\mathfrak{P}$, the mixture will remain at first in the state of a homogeneous liquid; when the temperature becomes equal to the abscissa of the boiling line the first bubble of gas will appear; that fraction of the mixture which

is in the gaseous state will increase with the temperature; at the moment when the temperature becomes equal to the abscissa of the dew line the last trace of liquid will disappear; the mixture will then remain homogeneous at all temperatures.

*If the pressure lies between the critical pressure* $\Pi$ *and the ordinate* $\pi$ *of the point* $Q$ the mixture will remain at first in the state of a homogeneous liquid. When the temperature becomes equal to the first abscissa of the boiling line, the first bubble of gas will appear; that fraction of the mixture which is in the gaseous state is at first an increasing function of the temperature; it passes then through a maximum and becomes a decreasing function; when the temperature becomes equal to the second abscissa of the boiling line the last trace of gas disappears; the mixture then remains homogeneous at all temperatures.

*If the pressure is greater than the ordinate* $\pi$ *of the point* $Q$ the mixture is homogeneous at all temperatures.

**B.**—*The critical point C lies upon the branch NR* (Fig. 12).

Let us suppose *that the mixture be compressed at constant temperature.*

*If the temperature is lower than the critical temperature* $\Theta$, the mixture is at first in the state of a homogeneous gas; when the pressure becomes equal to the ordinate of the dew line, the first drop of liquid appears; that fraction of the mixture which is in the liquid state is an increasing function of the pressure; when the pressure becomes equal to the ordinate of the boiling line the mixture is entirely in the liquid state; it remains then homogeneous under all pressures.

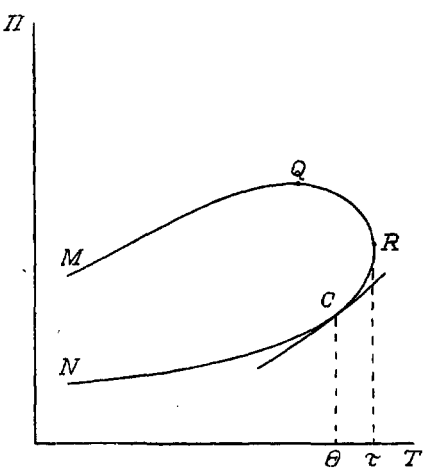

FIG. 12.

*If the temperature lies between the critical temperature* $\Theta$ *and the abscissa* $\tau$ *of the point R*, the mixture, under low pressures, is in the state of a homogeneous gas; at the moment when the point

($T$, $\Pi$) leaves the critical line it passes without discontinuity into the state of a homogeneous liquid ; the pressure, continuing to rise, becomes equal to the first ordinate of the boiling line, and at this instant the first bubble of gas appears ; that fraction of the mixture which is in the gaseous state is at first an increasing function of the pressure ; it passes next through a maximum and then becomes a decreasing function of the pressure ; when the pressure becomes equal to the second ordinate of the boiling curve, the mixture is again entirely in the liquid state ; it remains then homogeneous under all pressures.

*If the temperature is higher than the abscissa* $\tau$ *of the point* $R$ the mixture remains homogeneous under all pressures.

*If the mixture be heated under constant pressure* the phenomena observed will be the same as those noted under **A.**

Let us pass now to the Second Case, as defined upon page 287 without repeating, for this case, the reasoning which has been developed concerning the first. It will suffice to indicate the result to which the reasoning leads :

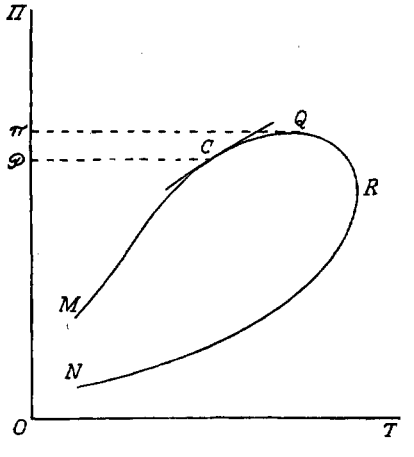


FIG. 13.

*The dew line and the boiling line meet at the critical point in such wise as to prolong each other; further, the dew line in setting out from the critical point rises, while the boiling line descends ; and, finally, at the critical point these two lines are tangent to the critical line.*

Let us consider (Fig. 13) the line $MQRN$ formed by the boiling line and the dew line. According to the foregoing proposition the critical point $C$ lies certainly upon the branch $MQ$.

*Let it be supposed that the gaseous mixture is compressed at a constant temperature;* exactly the same phenomenon will be observed as under the first case, **A.**

Suppose however *that the system is heated under a constant pres-*

*sure. If the constant pressure is less than the critical pressure* $\mathfrak{P}$, the mixture is at first entirely in the liquid state ; the temperature rises and reaches a value equal to the abscissa of the boiling line, and at this moment the first bubble of gas appears ; that fraction of the mixture which is in the gaseous state increases with the temperature ; when the temperature becomes equal to the abscissa of the dew curve the last trace of liquid disappears from the system, which then remains in the state of a homogeneous gas.

*If the constant pressure lies between the critical pressure* $\mathfrak{P}$ *and the ordinate* $\pi$ of the point $Q$, the mixture is at first homogeneous and gaseous ; the temperature, rising, reaches a value equal to the first abscissa of the dew curve, and at this moment a drop of liquid appears in the system ; the mass of the liquid is at first an increasing function of the temperature ; it passes then through a maximum and becomes a decreasing function ; when the temperature becomes equal to the second abscissa of the dew line the last trace of liquid disappears from the system, which then rèmains in the state of a homogeneous gas. *If the constant pressure is greater than the ordinate* $\pi$ *of the point* $Q$, the mixture remains homogeneous at all temperatures.

The three arrangements represented in the figures 11, 12 and 13 are realized for the mixture of ethane and of nitrous oxid recently studied by Kuenen ; one has to do with either one or another of these arrangements according to the value of the concentration.

It should be remarked, however, that these results can not be deduced solely from the general theorems concerning double mixtures, they require in addition a special hypothesis which has here been carefully emphasized.

It seems to me that these considerations, joined to the researches of van der Waals, to those of Kuenen and to my own early investigations, clear up completely the peculiarities which appear in the liquefaction of a mixture of two gases.

*Sept. 7, 1896.*