

8. Barotropic effect and gas-gas equilibria – Kamerlingh Onnes, Keesom, and Van Laar

8.1 *Historical setting – Keesom*

The Physics Laboratory in Leiden entered the 20th century in fine shape. Although the laboratory had lost the race for the liquefaction of hydrogen to Dewar in 1898, the technical advances made by Dewar, and in particular the invention of the double-walled, silver-plated vacuum glass that carries his name, were quickly incorporated into the instrumentation of the Leiden laboratory. Air and hydrogen liquefiers were under construction as an essential step towards the ultimate goal: the liquefaction of helium.

Once liquid hydrogen and a supply of pure helium gas became available by 1906, Kamerlingh Onnes and his group started preparing to take *PVT* data on hydrogen and helium at cryogenic temperatures, so that, with guidance from the law of corresponding states, an estimate could be made of the critical temperature of helium. While working with helium at liquid-hydrogen temperatures, Kamerlingh Onnes made a curious discovery. A vivid account of the discovery can be found in Kipnis (1996), p. 154-155. Here, we have followed the original papers and elaborate on the interpretation of the effect.

In this chapter, we meet a new player, destined to become the world's leading authority on the properties of helium at cryogenic temperatures. Willem Hendrik Keesom (1876-1956), a farmer's son from the island of Texel, began his physics studies at the University of Amsterdam and was a brilliant student. In 1904, he obtained his doctorate in Leiden with Kamerlingh Onnes. He held a research assistant position at the laboratory, where he was deeply involved in the preparations for the liquefaction of helium. From 1917 to 1923, he taught at the veterinary school in Utrecht. In 1923, he received a chair of experimental physics at Leiden University, and he succeeded Kamerlingh Onnes as the director of the Physics Laboratory. He was the first to solidify helium under pressure, in 1926. Over a period of time, he discovered evidence of a phase transition occurring in liquid helium at 2.19 K. In 1932, he measured, with Clusius, the lambda-shaped heat capacity anomaly of helium near

this superfluid phase transition. Keesom was elected to the Royal Netherlands Academy of Arts and Sciences (KNAW) in 1924, and to the Holland Society of Sciences and Humanities (HMW) in 1937.

Keesom's early work, in the time period covered in this book, concentrated on topics related to phase separation in fluid mixtures.

8.2 *A gas that sinks in a liquid*

8.2.1 *A curious experiment.* Kamerlingh Onnes (1906a) presented a two-page communication in the November Academy session about a strange phenomenon that he had observed. He was motivated by the following consideration. Suppose one pressurizes a system composed of a perfect gas and an incompressible liquid with negligible vapor pressure, and that the gas does not dissolve in the liquid. By pressurizing the system, it should be possible to increase the density of the gas enough to exceed the density of the liquid. If, initially, the gas was at the top of the vessel, it would end up at the bottom after enough pressure is applied.

Kamerlingh Onnes found such a system in fluids available to him: liquid hydrogen and compressed helium. He immersed a sturdy glass cell into a bath of boiling liquid hydrogen. The boiling point of hydrogen, 20 K, is far below the hydrogen critical point of 33 K, but far above the critical point of helium, which we presently know to be at 5.3 K. Kamerlingh Onnes filled the cell with a mixture of 6 parts hydrogen and 1 part helium. The system split into two phases, the liquid phase being mostly hydrogen and the vapor phase mostly helium. Kamerlingh Onnes then compressed the mixture. He noted that at 49 atmospheres, the gas phase sank and formed a large bubble at the bottom of the cell. Reducing the pressure to 32 atmospheres, he saw the bubble rise again. It was always clear which phase was the gas phase since the volume of the bubble decreased considerably with pressure, while the volume of the liquid was insensitive to pressure. Kamerlingh Onnes increased the pressure to 60 atmospheres, but the two phases remained.

Intuitively, the explanation of the sinking of the gas phase was relatively straightforward. The molecular weight of helium is twice that of hydrogen. By compressing the gas phase, consisting mostly of helium, one can make it denser than the liquid phase, mostly hydrogen.

Kamerlingh Onnes and Keesom (1906b), in the next Academy session, coined the term *barotropy* for the inversion of the phases. This paper is mostly descriptive. It speculates on the form of the isothermal transverse V - x plait in unit-mass coordinates, which must have a tie line parallel to the x -axis at the barotropic point, where the volumes per unit mass of the two phases are equal. At low enough temperature, however, when the plait runs

across the entire surface, the tie line must become parallel to the volume axis again at $x = 1$, so the system should re-invert at a second barotropic point. Thus, the authors are thinking mostly in terms of a transverse plait, although occasionally one finds an allusion to possible interference by a longitudinal plait.

The paper ends with an interesting question: what if the experiment would be done at a temperature where a solid phase appears? Would the solid phase, preponderantly hydrogen, float on top as the pressure increases? Schouten and Van den Bergh (1986) finally answered this question by studying a mixture of helium and hydrogen in a diamond anvil cell suitable for cryogenic work. Two diamonds, whose faces are separated by a gasket that forms the cell, are squeezed together, and high pressure is thus generated. The cell is the size of the head of a pin, and is observed under a microscope. Under appropriate conditions, the scientists observed three coexisting phases: a gas bubble, mostly helium, at the bottom; a mixed liquid phase, mostly hydrogen; and a tiny crystal of solid hydrogen floating at the top.

8.2.2 *Azeotropy and barotropy.* One could maintain that barotropy is just a curiosity, since a happenstance equality of mass density in two coexisting fluid phases does not seem to have any special physical significance. The chemical engineer who samples the wrong phase from a still because the phases have inadvertently switched positions might, however, be of a different opinion.

Van der Waals (1907) took an immediate interest in this discovery. His paper, presented in December, 1906, begins as follows 'Kamerlingh Onnes' startling experiment, in which a gas was obtained that sinks in a liquid....' He obviously did not consider it just a curiosity. On the contrary, he produced an elegant argument juxtaposing the cases of azeotropy and that of the sinking of a gas in a liquid. In the case of azeotropy, the two phases have the same mole fraction but different densities. The tie line is therefore parallel to the volume axis in the isothermal V - x plane, and so is the tangent at an azeotropic critical point. In the case of inversion of the phases, the two phases have the same mass density although molar density and mole fraction are different. If, therefore, mass units instead of molar units are used for volume and concentration, then at the inversion point the tie line is parallel to the mass fraction-axis, and so is the tangent at a plait point. The thermodynamic relations of the case of azeotropy, which Van der Waals (1890) developed earlier in his theory of mixtures, can be simply converted to those for the case of phase inversion by exchanging the volume and concentration variables.

No one will deny the significance of azeotropy in the case of fluid mixture behavior (see, for instance, Ch. 4.9, Ch. 5, Ch. 6.7, Ch. 7.2, Ch. 7.3, Ch. 7.4.3), nor its importance in the practice of distillation. Van der Waals

(1907) treated the two phenomena, azeotropy and phase inversion, on the same footing and thus gave azeotropy and barotropy equal fundamental significance. In the process, he developed the conditions for criticality of phases that have equal mass density.

8.2.3 *Quantifying the barotropic effect.* The Leiden researchers had a strong incentive to pursue this matter more deeply. Kamerlingh Onnes (1906a) mentions that even the sign of the parameter a for helium is unknown, and might even be negative, prohibiting liquefaction. From the paper by Kamerlingh Onnes and Keesom (1906b) it is clear that in December 1906, less than two years before the actual liquefaction of helium, they still did not have a reliable estimate of the helium critical temperature. If they could model the observed barotropic effect, that might give them an estimate. A paper by Keesom (1906) follows in the same session, in which such a model is presented. Interestingly, for this purpose the Leiden investigators, for the first time, turn to the Van der Waals equation for mixtures. To begin with, Keesom reformulates the Van der Waals equation for binary mixtures in terms of mass, instead of molar variables. In order to model the system helium-hydrogen, he chooses the molar mass ratio as 2, and assumes that the molar critical volume of helium is $1/4$ that of hydrogen. For this parameter choice, the Van der Waals equation predicts that there is a barotropic point on the gas-liquid plait around the boiling temperature of hydrogen, if the critical temperature of helium would equal $1/20$ that of hydrogen (roughly 1.5 K). A discouraging result indeed! Note, however, that this is a result applying to a transverse plait. At various instances, Kamerlingh Onnes and Keesom, however, do caution that a longitudinal plait might be present.

Keesom (1907) tries to find conditions for a barotropic plait point for the Van der Waals equation that give agreement with the observations of barotropy in the helium-hydrogen mixture. This study still limits itself to a transverse plait, but reference to possible interference with a longitudinal plait is frequent. What values to use for the a and b parameters turns out to be a difficult question. In a 1 $1/2$ page footnote, Keesom struggles to find a and b parameters suitable for describing known hydrogen and helium properties, while giving results compatible with the barotropic experiment, in an effort to estimate the critical temperature of helium.

As in his previous paper, Keesom begins with an excluded volume for helium that is $1/4$ of that of hydrogen per mole ($1/8$ per unit mass), but also tries a value twice as large. What to choose for the value of a for helium is unclear. Keesom expects that the cohesion of helium is very small, and realizes that in that case Van der Waals's mixture equation would give rise to a longitudinal plait. Another unknown in the problem is the composition

dependence of the excluded volume for helium-hydrogen. Even with that many adjustable parameters, it is not possible to make sense of the meager experimental evidence under the hypothesis that there is a transverse liquid-vapor plait. Upper bounds for the helium critical temperature in the paper range from $1/175$ to $1/4$ of the critical temperature of hydrogen, rendering them useless. In writing this paper, however, Keesom is gradually acquiring the insight that the presence of a longitudinal plait must be considered. Further work with Kamerlingh Onnes elucidates what the nature might be of the phase diagram helium-hydrogen (Sec. 8.3).

A final remark about barotropy: this is a phenomenon more general than that of 'a gas sinking in a liquid.' If two liquid phases of almost the same mass density but of different compressibility coexist, a change of pressure can easily lead to phase inversion, to no one's surprise. Historically, however, this feature was first discovered in the more spectacular case of 'a gas sinking in a liquid' and was connected with phase separation in the gas phase.

A reliable value for the critical temperature of helium would be obtained later in 1907, after the first P - V - T data for helium at temperatures around 20 K became available. Using the law of corresponding states and mapping the helium isotherms onto those of hydrogen, Kamerlingh Onnes (1907e) obtained an estimate of 5.3 to 6 K for the critical temperature of helium. As narrated in Sec. 3.3, this estimate enabled the designing and dimensioning of a helium liquefaction apparatus; helium was first liquefied on July 9, 1908.

8.3 *Gas-gas separation*

The Leiden work now takes a different turn. In the next few papers, Kamerlingh Onnes and Keesom (1907a, 1907c; Comm.Leiden Suppl. 15) elaborate on the idea of a mixture in which one component has no cohesion, and investigate the phase behavior of a Van der Waals mixture with $a_2 = a_{12} = 0$. That is, the second component exerts no attractive interactions whatsoever, but *does* have a finite excluded volume. Here subscript 1 refers to the component representing hydrogen, and 2 refers to the component without cohesion, representing helium. In the K&S global phase diagram for equal excluded volumes, Fig. 7.2, this case would correspond with $\zeta = 1$, $\Lambda = 1$. It does fulfill the geometric-mean condition for the attraction.

Contrary to the experiences of Korteweg (Ch. 5, Ch. 7.3) and Van Laar (Ch. 7.5), who ended up with complex models requiring extensive formula manipulations, the two Leiden scientists invented a model that they could handle readily. It shows some interesting physics. There is at most one plait on the isothermal Helmholtz energy surface, a plait that is neither purely transverse, nor purely longitudinal. The second component has no critical

point, so no plait can begin or end there. The two coexisting phases can be considered to both being gas phases, since they may occur above the critical temperatures of both components. In the spring of 1907, the two scientists reached a full understanding of the behavior of the gas-gas plait for the Van der Waals binary mixture.

The 1907a paper begins on a provocative note. First of all, there is a three-line footnote referring to the Van Laar (1905c,d) paper that contain the exact expression for the plait point curve, as discussed in Ch. 7.5.4. The footnote states:

Van Laar treated the projection of the plaitpoint curve on the v, x plane for such a mixture, without, however, further investigating the form of the spinodal curve and of the plait.

This is a rather grievous understatement of the work of Van Laar, who will not take this remark lightly (see below). The Leiden authors further ignore Van Laar's work, and base themselves solely on the Van der Waals (1890) mixture paper.

In the second paragraph Kamerlingh Onnes and Keesom (1907a) state:

Two different phases may be in equilibrium which must both be considered as gasphases. Then the two substances which are the components of these mixtures are not miscible in all proportions even in the gas state.

The italics are theirs. Here we see two good advertisers at work: this sentence is bound to catch the eye of the reader.

Another footnote on the first page refers to an Academy paper by Van der Waals (1894d). In this brief paper (in Dutch) Van der Waals indeed postulates that there might be a longitudinal plait on the Helmholtz-energy surface at temperatures exceeding the critical temperatures of the two components, so that there is no transverse plait on the surface. He expects that this could happen when 'the mixing takes a lot of energy' presumably because the cohesion between unlike components is much weaker than that of each of the components. For Van der Waals's description of the birth and growth of the longitudinal plait, the reader might refer to a picture from Korteweg's work for the symmetric case, see Fig. 7.7 (GTP A₁). This plait moves into the surface from the 'side of the small volumes', $V = b_x$, where the pressure is infinite. Once formed, well above the critical temperature of the components the plait proceeds into the V - x plane towards the larger volumes as the temperature is lowered. It begins at the temperature at which the plait point appears on the line $V = b_x$. We recall that this 'third critical temperature' was introduced earlier by Van der Waals (1890) in his Appendix, as well as by Korteweg (1891b).

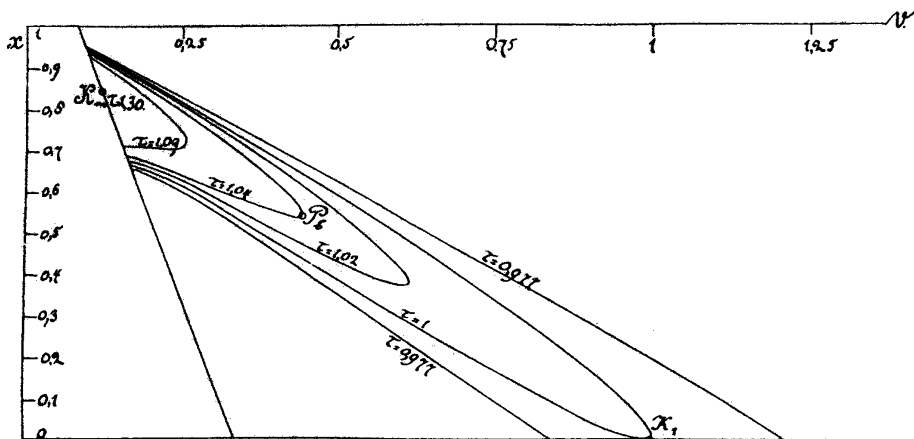


Figure 8.1 The gas-gas plait for a binary mixture, one component having no cohesion. Copied from Kamerlingh Onnes and Keesom (1907a), Plate I, Fig. 1. Several isothermal spinodals are indicated, each labeled with its value of the reduced temperature $\tau = T/T_{K_1}$. The plait starts at K_m , and moves into the V - x surface as the temperature drops. The plait point leaves the surface at K_1 , the critical point of the component that does have cohesion.

Van Laar (1905b, 1905d) used it extensively in his analysis of the various types of phase diagrams, as discussed in Ch. 7.5.4.

In their treatment of the case where one component has a non-zero excluded volume but no cohesion, the two Leiden scientists begin with their version of the Van der Waals equation in mass units, for a molar mass ratio of 2 and a molar volume ratio of 1/4 between the first and second component. Only the first component has a nonzero value of a , and the quadratic mixing rule, Eq. (4.5), is used to calculate a_x . The value of b_x is linearly interpolated between the excluded volumes of the two components. They use the Van der Waals (1890) expression for the spinodal, substitute the chosen values for the parameters, and obtain a relation cubic in volume and mass fraction, and linear in temperature. They solve this equation numerically and obtain the spinodals shown in Fig. 8.1 for a variety of temperatures. The result is a plait running at an angle through the V - x plane. The plait point begins at K_m , their symbol for the third critical temperature, which in this case equals 1.30 on a reduced scale, and ends at the critical temperature of the first component. The plait moves into the plane as the temperature falls. Once the plait point reaches the critical point of the first component, it leaves the surface, and only an open plait is left. Fig. 8.2 shows the progression of the plait in P - x coordinates.

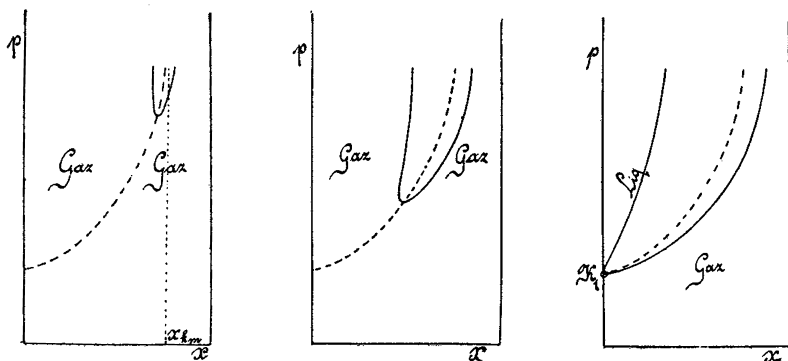


Figure 8.2 A schematic of the gas-gas plait in the pressure-mass fraction plane. The plait moves to the pure-component critical point as the temperature decreases. Dashed curve: projection of the critical line. Full curves: isothermal connodals. Copied from Kamerlingh Onnes and Keesom (1907a), Plate 1 Figs. 3-5.

On the open plait near the critical point of the first component, the two coexisting phases differ in density, and it is still sensible to distinguish a vapor and a liquid phase, even though the temperature may be above the critical temperature of the only component that has a critical point. Near the third critical temperature, however, the phases are both near the close-packed state and differ mostly in mass fraction. The character of the plait thus changes from mostly transverse at the first component's critical point to mostly longitudinal near the close-packed state.

Our Leiden heroes, however, spend many pages arguing that both phases should be called gas phases. At first they use the following criterion: the name gas or liquid is appropriate only if the particular phase can be connected without a phase transition along an isobar or isopleth (curve of constant concentration) to another phase for which the designation gas or liquid is clear. The authors seem to get trapped in convoluted semantics, but finally propose another criterion: that the plait must occur at temperatures above the critical temperatures of both components. The term gas-gas equilibrium is indeed still in use for this case.

In the last part of the paper, presented on March 30, 1907, the authors relax the condition of zero cohesion, and just make the cohesion a_{22} very small. They decline to discuss the complications induced by the presence of the additional critical point for the weakly cohesive second component, referring to Van Laar (1906a, 1906b) in a footnote, but without any discussion of the quoted work. They then discover that the gas-gas plait may split, one part coming in from the critical point of the first component, the other

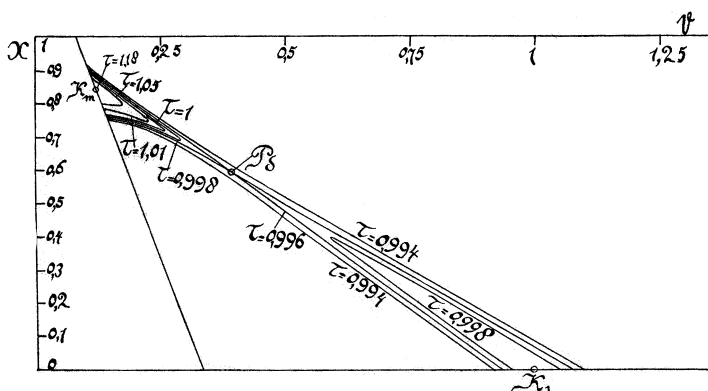


Figure 8.3 The gas-gas plait in the case that one component has small, but nonzero cohesion. Isothermal spinodals are shown, each labeled with the value of $\tau = T/T_{K_1}$. Plaits now enter from K_m and K_1 , and meet at a homogeneous double plait point as the temperature decreases. Copied from Kamerlingh Onnes and Keesom (1907a), Plate II.

part from the line $V = b_x$. As the temperature decreases, the two plaits meet in a homogeneous double plait point, at a temperature minimum, Fig. 8.3. They calculate the conditions for the minimum in terms of the interaction parameters of the two components. They do cite Korteweg in connection with the meeting of the two plaits in a homogeneous double plait point. What is missing from this paper is a connection with previous work by Kuenen, as well as by Van Laar, discussed in Ch. 7, on systems that have a plait point curve running to high pressures. Although Van Laar's (1906a, b) work is cited, it is brushed aside as not relevant to a component with feeble attraction. Shortly after, the authors will receive a forceful reminder of this omission.

8.4 *Matters of priority – Van Laar, Kamerlingh Onnes and Keesom*

A pained reaction by Van Laar (1907a) was presented to the Academy by Lorentz one month after the second of the Kamerlingh Onnes and Keesom (1907a) papers had been communicated. Van Laar wrote the bulk of his paper after he had read the February 23, 1907 presentation (§I-§6), but before he read that of March 30 (§7). Van Laar must have hastily composed this 13-page paper. The large number of typos and aggrieved tone, in addition to the content, point to considerable mental anguish on the part of the author.

In a footnote, Van Laar criticizes the use of the term gas-gas equilibrium for two obviously quite dense phases. He proposes to use Van der Waals's term 'fluid phases.' Van Laar has a point, but history will not be on his side.

Van Laar reminds Keesom that if the cohesion of the second component is weak, the phase diagram is more complicated than the single simple plait the Leiden scientists show, because the volatile component now has a critical point, with a three-phase region nearby.

In the first few pages, Van Laar claims priority regarding the plait described by Kamerlingh Onnes and Keesom (1907a). Keesom's application, with $a_{22} = a_{21} = 0$, is indeed a special case of Van Laar's geometric-mean Van der Waals mixture model, so Van Laar's point seems well taken. In a footnote, Van Laar refers to half a dozen papers from his hand, written in 1905 and 1906. Several of these were discussed in Ch. 7.5.

We recall how Van Laar showed that the two parts of the V - x projection of the plait point line exchange connectivity at a special condition of the interaction parameters (Ch. 7.5.5). If the critical temperature ratio is larger than that corresponding to what we now call the Van Laar point, a plait point curve will run from the plait point of the least volatile component, C_2 , to the 'third critical point' C_0 at $V = b_x$, resulting in what we presently call a Type-III phase diagram (Fig. 7.4). Van Laar himself was fully aware, and mentions again here, that the experimental systems water-ether and ethane-methanol are of this type. He also showed that this feature persists, even when the excluded volumes are unequal. The peculiar limiting case of one component with zero cohesion and therefore no critical point, he writes, may have led to failure on Kamerlingh Onnes's and Keesom's part to connect with Kuenen's and Van Laar's vl Type-I, presently called Type-III phase behavior.

Van Laar is very insistent on a particular aspect of the plait: will this plait run from C_0 to C_2 , (or from K_m to K_1 , in Fig. 8.1), as discussed by Keesom? Or could it start as two plaits moving from each end towards each other and meeting in a double plait point somewhere in the middle of the V - x plane? If the latter is the case, the plait point curve from K_1 to K_m (from C_2 to C_0) must pass through a temperature minimum. This minimum, where the two parts of the plait meet, is clearly visible in Van Laar (1905d), Fig 1, reproduced in this book in Fig. 7.19. See the two isothermal spinodals join barely below C_0 , in the top left figure, for $\varphi = 1$. Van Laar (1905e) also specified conditions on the ratios of critical pressures and critical temperatures of the two components for the minimum to occur. Unfortunately, the precise location of the minimum, topic of a paper Van Laar (1906a) had submitted to Archives Teyler, was not yet in print when the Kamerlingh Onnes and Keesom (1907a) paper appeared (although the Leiden scientists did cite it, but considered it not relevant). So, in a rush, Van Laar (1907a)

summarizes the Archives Teyler paper in seven or eight pages of dense formulae and calculations.

Van Laar (1907b) added an appendix to his paper after he read the March 30 presentation of Kamerlingh Onnes and Keesom (1907a). For the more general case that a_{22} is small but not zero, the Leiden authors indeed discovered that there is a minimum in the plait point curve, and derived an expression for it. This obliterates part of Van Laar's criticism in the body of his paper. Van Laar (1907b), however, demonstrates in his Appendix that he derived this identical expression a year earlier, see Van Laar (1905g), and mentions that Verschaffelt (1906a) confirmed this result shortly after.

A reply by Kamerlingh Onnes and Keesom (1907c) was not long in coming. Half the first page of their paper is occupied by lengthy footnotes disputing Van Laar's criticisms. They do not agree with his objection to the terminology gas-gas. They feel they did sufficient justice to Van Laar's work on the three-phase equilibrium in the VL Type-I phase diagram by citing a reference to his papers in the last part of their criticized paper. For the 'critical point of complete miscibility' (Van Laar's third critical temperature) they credit Van der Waals (1890). Then they point out that Van Laar treated only one case of a gas-gas line, namely that with a minimum in temperature. In a lengthy discussion demonstrating their familiarity with Korteweg's theory of plaits, they argue that there are several cases with no minimum in the plait, one of which having been discovered by themselves, but overlooked by Van Laar.

In a remarkably meek reply, Van Laar (1907b) concedes the points made by Kamerlingh Onnes and Keesom, and generously acknowledges (in a footnote in the English version of the Proceedings) the priority of Kamerlingh Onnes and Keesom in recognizing different ways the plait may run to the third critical point. Half a page of errata to his preceding paper appears at the end of this paper. These do not refer to typos, but to issues of substance resulting from Van Laar's haste in producing the 1907a paper.

The last paper in the sequence by Kamerlingh Onnes and Keesom (1907d) combines the two themes: barotropy, and mixtures in which one component has only feeble cohesion. It is a very detailed investigation of the kinds of plaits that show barotropy. We will not discuss this paper here, but only mention that constructive references to Van Laar's work are now plentiful and generous, giving Van Laar credit where credit was clearly due.

8.5 *Measuring gas-gas equilibria*

According to their own principles, Kamerlingh Onnes and Keesom had not measured gas-gas separation. This term refers to the case that the plait exists

above the critical temperatures of both components. The Leiden scientists, however, measured the phase separation in the helium-hydrogen system at the hydrogen boiling point, well below the critical point of hydrogen but far above that of helium.

It is common for the critical line to move through a minimum temperature for systems that display this kind of separation. Consequently, a high pressure is needed to then bring the mixture critical temperature to higher values than the critical temperature of the least volatile component.

Krichevskii and Tsiklis (1941) first measured gas-gas separation in the system nitrogen-ammonia. It took a pressure of over 9500 atmospheres to bring the mixture critical temperature above the ammonia critical temperature.

8.6 *A case study of the workings of the Dutch School*

The short episode, less than a year, in which the phenomenon of barotropy was discovered, explained, and generalized to gas-gas equilibrium, provides an interesting example of the mode of operation of the Dutch School. Kamerlingh Onnes himself performed the innovative experiment: compressing a mixture of two components of very different volatility, hydrogen and helium. To explain the existence of a plait persisting to high pressures, Kamerlingh Onnes and Keesom used the 1890 paper by Van der Waals in a straightforward and effective way. In the process, they intruded on territory recently occupied by Van Laar. Van Laar then overreacted, writing a substantial paper before he had completely read the Leiden scientists's paper. Kamerlingh Onnes and Keesom were in good command of all issues, and had indeed found variants of what they called the gas-gas plait that Van Laar had overlooked. The episode ended in harmony, and on a rare conciliatory note by Van Laar. This episode had a high level of intellectual intensity, as evidenced by the large number of academy presentations in such a short time span.

Amidst all this commotion, what was Van der Waals's role? Apparently, his only contribution was the very nice paper on the analogy of azeotropy and barotropy, which we discussed. Throughout these stormy discussions about the plait running to infinite pressure, while his name was invoked repeatedly, Van der Waals plowed away at a five-part series of substantial papers on the theory of binary mixtures and stayed out of the fray.