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A gas that sinks in a liquid—the first helium experiment published by Kamerlingh Onnes*

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Received 22 January 2009

Published 31 March 2009

Online at stacks.iop.org/JPhysCM/21/164222

Abstract

The year 1906 was a year of many remarkable achievements in the laboratory of Kamerlingh Onnes and his staff. They put into operation a hydrogen liquefier producing 4 l h^{-1} , followed by a liquid-hydrogen cryostat for work below 21 K. They prepared their first sample of 2 l of helium gas. Pressure–volume–temperature measurements down to 54 K were in progress for hydrogen, and initiated for helium, in order to obtain an estimate for the critical temperature of helium; this estimate was urgently needed for design of a helium liquefier. Towards the end of 1906, Kamerlingh Onnes performed the first helium experiment at liquid-hydrogen temperature: a test of the phase behaviour of a mixture of hydrogen and helium. In the process, he discovered what he termed the barotropic effect: at increasing pressure, the helium-rich vapour phase sank to the bottom, having become heavier than the hydrogen-rich liquid phase. This paper describes the experiment and the resulting flurry of activity by Van der Waals, Kamerlingh Onnes, Keesom and Van Laar, all trying to understand and model the curious phase behaviour, as well as earlier relevant work by Van der Waals, Korteweg, Kuenen and Van Laar.

1. Introduction

1.1. Historical setting

The year 1906 was a particularly rich and rewarding year on the path towards liquefaction of helium at the Leiden Physical Laboratory. Since Dewar had liquefied hydrogen in 1898, Director Kamerlingh Onnes (1953–1926) had focused on the construction of a hydrogen liquefier that could produce several litres of hydrogen per hour. The design was modelled after that of Linde and Hampson: pressurized hydrogen gas is first precooled by liquid air, cooled further in a recuperative heat exchanger, and finally expanded through a throttle valve. After disappointing earlier attempts, in February 1906 Kamerlingh Onnes and his staff triumphantly started operating the new liquefier. It produced 4 l h^{-1} , an unprecedented yield. The next day, Kamerlingh Onnes took a glass Dewar containing 4 l of liquid hydrogen to the meeting of the Royal Netherlands Academy of Arts and Sciences (KNAW), presumably by train.

This achievement set the stage for the next goal: building a helium liquefier based on the same principle, but this time hydrogen is used to cool helium below its inversion temperature. The first hurdle was, of course, to obtain enough helium to liquefy not just a few drops, but an appreciable quantity. Although helium had been discovered in the spectrum of sunlight as early as 1868, only in the 1890s was it discovered on earth, in mines in the US. In the felicitous year 1906 Kamerlingh Onnes prepared his first few litres of pure helium gas from a load of monazite sand shipped from the US. The second hurdle was the lack of a reliable estimate of the critical temperature of helium. Kamerlingh Onnes' plan was to use Van der Waals' law of corresponding states, comparing pressure–volume isotherms of hydrogen and helium from 373 down to 54 K (the lowest temperature reachable by reducing the pressure of a liquid-oxygen bath). In 1906, the programme was well under way for hydrogen, and it was initiated for helium as soon as the first sample of the gas became available. Although this phase of the work did not require a hydrogen cryostat, one was completed in 1906 anyway, in the expectation that it would be needed eventually.

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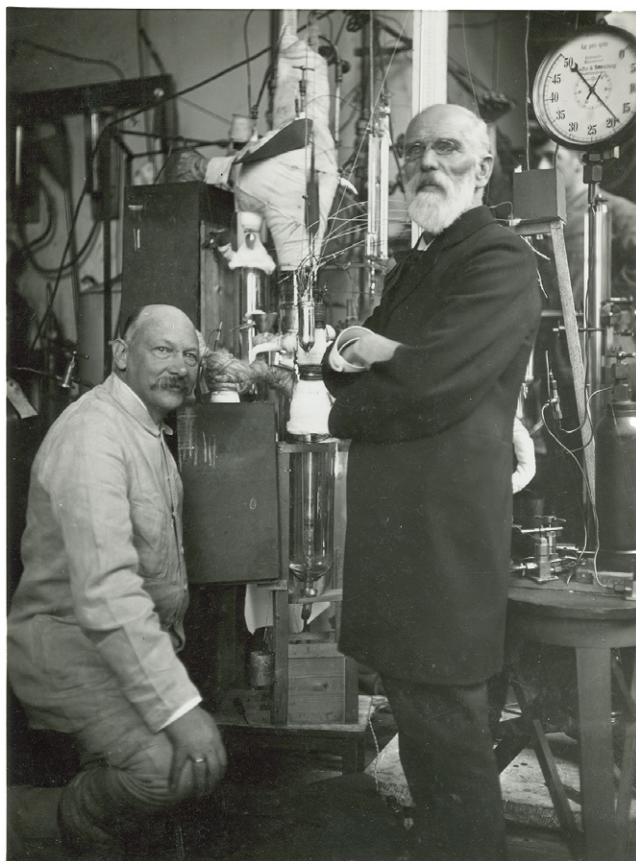


Figure 1. Kamerlingh Onnes (left) and Van der Waals posing by the helium liquefier in 1911. Photograph courtesy of the Leiden Academisch Historisch Museum, reprinted with permission.

1.2. The 1873 Van der Waals equation and the law of corresponding states

Their famous joint portrait that includes the helium liquefier, figure 1, reminds us of Kamerlingh Onnes' acknowledgement, in his Nobel Prize speech of 1913, that he could not have liquefied helium without the law of corresponding states. Van der Waals formulated this law in 1880 on the basis of his equation of state:

$$[P + a/V^2][V - b] = RT. \quad (1)$$

Here, P is the pressure, V the molar volume, T the absolute temperature and R the molar gas constant. The parameter a characterizes the molecular attraction, while b represents the volume excluded by the finite size of the molecules. When $V = b$, the system is close packed and the pressure is infinite. The Van der Waals (VdW) equation was the first to display a vapour–liquid phase transition and a critical point. Only below the critical temperature could the fluid be liquefied. The critical parameters P_c , V_c and T_c can all be expressed in terms of the parameters a , b and R . For instance, the critical volume equals $3b$. With the critical parameters as units of pressure, temperature and volume, the resulting reduced VdW equation becomes universal: the law of corresponding states. The theoretical shortcomings of the VdW equation were well recognized around 1906, and it was

known that its accuracy left much to be desired. Kamerlingh Onnes had, however, shown as early as 1881 that the principle of corresponding states is more general than the specific Van der Waals equation, as a consequence of the fact that only two parameters are used to characterize individual gases.

2. The first helium experiment reported by Kamerlingh Onnes

In November 1906, amidst the pressing work ongoing in his laboratory, we find Kamerlingh Onnes itching to try out a novel scientific experiment, using liquid hydrogen and his first supply of helium. Imagine, he proposes, a pressurized mixture of helium and hydrogen gas, cooled to the boiling point of hydrogen, 20 K, well below the hydrogen critical temperature, but well above the still unknown critical temperature of helium. Presumably, the mixture would phase-split, forming a helium-rich vapour phase and a hydrogen-rich liquid phase. Now consider pressurizing this mixture further. The vapour phase being quite compressible, it is thinkable that it might become denser than the hardly compressible liquid phase. The results of the experiment are described in an elated three-page note 'A gas that sinks in a liquid', presented at the Royal Netherlands Academy of Arts and Sciences (KNAW) in November 1906 [1]. He used his greatly improved Cailletet mercury compressor, see [2 chapter 14], to pressurize the mixture. He introduced the mixture into a glass tube which was immersed in liquid hydrogen; it had a capillary inflow tube at the top and an outflow tube at the bottom. 'Up to 49 atmospheres, the liquid hydrogen was seen to deposit from the gas mixture, bounded by a distinct hollow meniscus against the helium. At 49 atmospheres, the helium, or, properly speaking the gas phase consisting chiefly of helium, went down just as water through oil, and remained on the bottom as a large drop. With further compression to 60 atmospheres and decrease of pressure to 32 atmospheres the volume of the bubble appeared to follow the change of the pressure as that of a gas. At 32 atmospheres the bubble rose again. By changing the pressure the bubble was made to rise and descend at pleasure'. (I have reproduced the original units. 1 atmosphere equals 0.101 325 MPa.) My cartoon, figure 2, illustrates what he observed. Kamerlingh Onnes coined the phenomenon of the inversion of phases a 'barotropic point'. Phase inversion due to difference in the thermal expansion coefficient was known in density-matched partially miscible binary liquid mixtures but this was the first time an inversion was observed in what was considered a vapour–liquid system. Incidentally, the mixture did not indicate the presence of a critical point up to the maximum pressure employed.

3. Modelling the system helium–hydrogen—why?

Kamerlingh Onnes now possessed a new and possibly relevant piece of information about the mixture of hydrogen and helium. At 20 K, at known overall concentration, and around 50 atmospheres, the two coexisting phases have the same density. If he could model the properties of the mixture, perhaps it would give him the chance to estimate

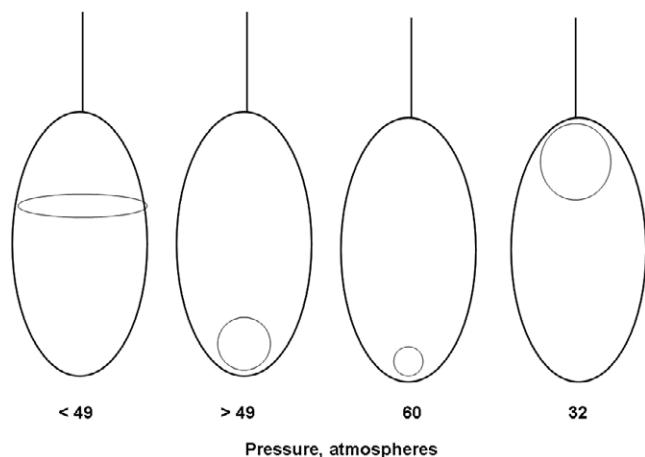


Figure 2. My cartoon, not to scale, of the experiment ‘a gas that sinks in a liquid’, as described by Kamerlingh Onnes [1]. For a helium–hydrogen mixture of 0.2 mole fraction helium, maintained at 20 K, the gas phase becomes heavier than the liquid phase at a pressure exceeding 49 atmospheres (1 atmosphere equals 0.101 325 MPa). The volume of the compressible gas bubble decreases with pressure.

the critical point of helium, which might mean a shortcut compared to the tedious process of PVT measurements that was already in motion. It was clear that he needed help in constructing such a model. So he engaged his postdoctoral research associate, Keesom (1876–1956), who was destined to measure the lambda-shaped heat capacity of helium in Leiden a quarter-century later. Around 1900, the Dutch School was the world leader in the measurement and understanding of phase behaviour of fluid mixtures. In particular, Van der Waals had formulated a binary-mixture equation of state in 1890, while the Leiden group, including Keesom, had made important experimental discoveries regarding phase separation in mixtures from 1891 onwards. So we shall now backtrack and summarize what was known about binary-mixture phase behaviour at the time of the November 1906 experiment.

4. Phase behaviour of binary mixtures—the Van der Waals model

4.1. The Van der Waals (VdW) equation of state for binary mixtures

The foundation for the phase separation of mixtures was laid in the mid-1870s by Gibbs, with whose work the Dutch School was thoroughly acquainted. In 1890 [3], Van der Waals generalized his equation of state (1) for application to binary mixtures, as follows:

$$[P + a(x)/V^2][V - b(x)] = RT, \tag{2}$$

with x the mole fraction of the second component. Van der Waals gave the following prescriptions for the dependence of $a(x)$ and $b(x)$ on x :

$$a(x) = a_1(1 - x)^2 + 2a_{12}x(1 - x) + a_2x^2; \tag{3}$$

special case: $a_{12}^2 = a_1a_2$, geometric-mean rule;

$$b(x) = b_1(1 - x)^2 + 2b_{12}x(1 - x) + b_2x^2;$$

special cases: $b = \text{constant}$, or b is linear in x . (4)

Interesting and complicated phase separations result for a_{12} relatively weak compared to a_1 and a_2 , each component preferring its own company over that of the other. Van der Waals obtained the following important results for his mixture equation of state.

- (1) It produces liquid–vapour phase separation and criticality.
- (2) It produces additional phase separation and criticality in liquid or dense phases.
- (3) Phase separation in the dense phase can occur above the critical points of the two components if a_{12} is sufficiently weak.
- (4) The equation produces three-phase equilibrium, liquid–liquid–vapour.
- (5) The equation can produce azeotropy: a locus of coexisting phases with the same concentration.

The VdW mixture equation has such virtues that, over a century later variants under the general flag of ‘cubic equations’ are still the unsurpassed means for describing phase separation of multicomponent mixtures in the petroleum industry. Though not yielding good liquid densities, they give realistic phase diagrams. They provide a trustworthy estimate of the phase behaviour, before more sophisticated approaches are tried that may suffer from spurious extrema in the unstable region.

4.2. Phase behaviour of a Van der Waals mixture of two identical components—Korteweg

Korteweg (1848–1941), figure 3, the first professor of mathematics at the University of Amsterdam, is best known for the Korteweg–de Vries equation for the propagation of solitons. He was the thesis adviser of perhaps the most famous mathematician in the Netherlands, the intuitionist Luitzen Brouwer. It is less known that Korteweg obtained his doctorate with Van der Waals, for lack of a mathematics professor at the young University of Amsterdam, and that he worked for several years on the mathematical foundation of folds on surfaces, as well as on a specialized VdW binary mixture. Korteweg’s two major papers on these topics appeared in French, along with the French translation of the VdW mixture paper, in Archives Néerlandaises in 1891 [4a, 4b]. Korteweg’s model was that of two identical components, having the same a , b , and critical temperature. The excluded volume parameter is a constant, but the interaction parameter between the two components is chosen smaller than a , which leads to surprisingly complex phase behaviour. Here we produce some pictorial results [4b] of his calculations that illustrate the properties of the VdW mixture equation outlined in section 4.1. In this and subsequent diagrams, all taken from the original papers, some labels may have been added for clarity, and several pictures have been rotated so that the volume ranges from small (or close-packed) on the left, to volumes exceeding the critical on the right. The concentration runs from



Figure 3. Korteweg, around 1896, professor of mathematics at the University of Amsterdam. Photograph courtesy of Bastiaan Willink, his great-nephew, reprinted with permission.

component 1 (bottom) to component 2 (top). Unless stated differently, all figures are for constant temperature.

Figure 4, top, is for a case in which a_{12} is quite small. The close-packed volume $V = b$ is on the left, and the critical volume, $V = 3b$, is indicated. Around $V = 3b$ there is no phase separation at $x = 0$ or 1, so the two identical components are above the critical temperature. Nevertheless, there is phase separation in the dense phase near $V = b$. The dark region is that where the homogeneous fluid is unstable, and the coexisting phases (which are on a stable part of the surface) are indicated by a curve, the ‘connodal’ or coexistence curve. ‘Tie-lines’ connect coexisting phases, and those in this case are vertical because of the symmetry of the system. This thermodynamic instability of the mixture in the dense state was called a ‘longitudinal plait’ by the Dutch school. Because the word ‘plait’ misleads native English speakers, I will call it a ‘fold’. The fold retracts to the left as the temperature increases, and leaves the surface at some finite temperature, which Van der Waals had coined the ‘critical temperature of complete miscibility’.

Figure 4, bottom, at a somewhat larger value of a_{12} and at a lower temperature, shows a system below the critical temperature of the components. A region of instability, causing vapour–liquid phase separation, extends from $x = 0$ to 1, and is called a ‘transverse’ fold. In addition, there is a longitudinal fold, as before. The two folds interact. Coexisting phases for each fold are indicated, and the triangle shows coexistence of two dense, liquid-like phases, in addition to a large-volume gas phase. This completes the illustration of properties 1–4, section 4.1, of the VdW mixture equation.

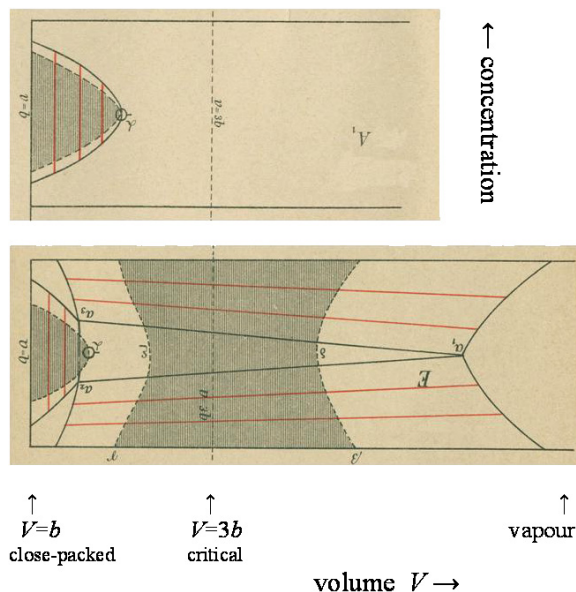


Figure 4. In an isothermal mole fraction x versus molar volume V diagram, Korteweg [4] sketches phase separation in a binary Van der Waals mixture of *identical* components with weak mutual attraction. In the dark areas, the mixture is unstable. Top: a case of phase separation in the dense phase above the critical points of the components: a ‘longitudinal fold’. Bottom: below the critical temperature of the components: both a ‘transverse’ vapour–liquid fold and a longitudinal fold, interacting to create the three-phase equilibrium indicated by the triangle. For further details, see section 4.2. Reproduced with permission from [5]. Copyright 2002 KNAW.

(This figure is in colour only in the electronic version)

4.3. Phase behaviour of binary mixtures—experiments by Kuenen

When Van der Waals’ work on the mixture equation was nearing completion, Kamerlingh Onnes decided to start a series of experiments to test the predictions of the theory. He engaged a brilliant young graduate student, Kuenen (1866–1922), for this task. In a quick succession of experiments in the early 1890s, Kuenen proved himself a wizard in experimentation, in full command of Gibbs’ thermodynamics and of Van der Waals’ subsequent theory of mixtures. He was the first in the world to produce reliable data for vapour–liquid equilibrium in pressurized mixtures, namely by installing a stirrer in his cell. He is best known for his discovery of ‘retrograde condensation’, the appearance of a liquid phase in an isothermal mixture on *release* of the pressure, a phenomenon that would become a major headache for the gas and oil industry in the 20th century. Although this mixture behaviour is implicit in the VdW equation, Kuenen was the first to realize it, claiming priority to the annoyance of Van der Waals. Kamerlingh Onnes took the side of his graduate student against his close friend, which resulted in a cooling of his relation with Van der Waals for several years; see [5 chapter 6]; [2, chapter 18].

The experiments that illustrate aspects of Van der Waals’ theory and are relevant to the present story are the following: the phase separation in $\text{CO}_2\text{--CH}_3\text{Cl}$, both below and in

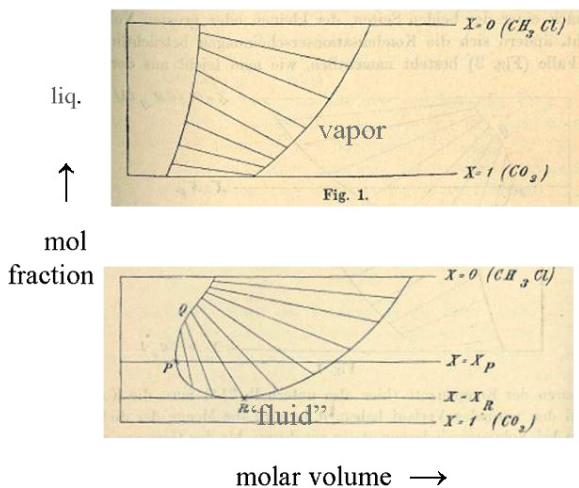


Figure 5. Kuenen’s phase separation experiment [7] in the binary mixture of CO₂ and CH₃Cl in x - V coordinates. CO₂, at $x = 1$, is the more volatile component with the lower critical temperature. Top: an isotherm below the critical temperatures of both components. A ‘transverse fold’ separates coexisting liquid and vapour. Tie-lines connect coexisting phases. Bottom: an isotherm between the critical temperatures of the components. The fold terminates at a mixture critical point. Reprinted from [7] with permission.

between the critical temperatures of the two components [6, 7]; and that in C₂H₆-N₂O, in which critical azeotropy was discovered [8]. Figure 5 illustrates the first experiment. As before, the diagrams are mole fraction x versus molar volume V diagrams for isothermal phase separation. The concentration

ranges from the pure more volatile component (CO₂) at $x = 1$ (bottom) to the pure less volatile component at $x = 0$ (top). In the top diagram the system is below the critical points of the two components, as well as of the mixtures in between. Consequently, on the $x = 0$ and 1 axes, as well as at mole fractions in between, there is an unstable region, and the mixture splits into two phases, a liquid phase to the left and a gas phase to the right of the two-phase region in figure 5. At $x = 0$ and 1, the tie-line is parallel to the volume axis because vapour and liquid have the same concentration. In the mixtures, the tie-line tilts, because the vapour phase contains more of the volatile component. Figure 5, bottom, illustrates what happens if the temperature of the diagram is *between* the critical temperatures of the two components. Now, there is no phase separation at $x = 1$ (the more volatile component, CO₂), but there is at $x = 0$. Thus, the fold originating at $x = 0$ has no boundary to terminate on, and therefore has to close somewhere in the middle of the diagram. In the point P the tie-line, at a finite angle, shrinks to a mixture critical point. On further increase of temperature, the fold would shrink and retreat, to disappear at the critical point of the least volatile component.

There is a different way in which a fold can disappear from a surface. This is illustrated in Kuenen’s second experiment: phase separation in a mixture of nitrous oxide and ethane (figure 6). The two components have critical temperatures that are close together, and the mixture critical locus passes through a minimum in temperature. At a temperature below the minimum on the critical locus, there is vapour-liquid phase separation all across the concentration range, as before

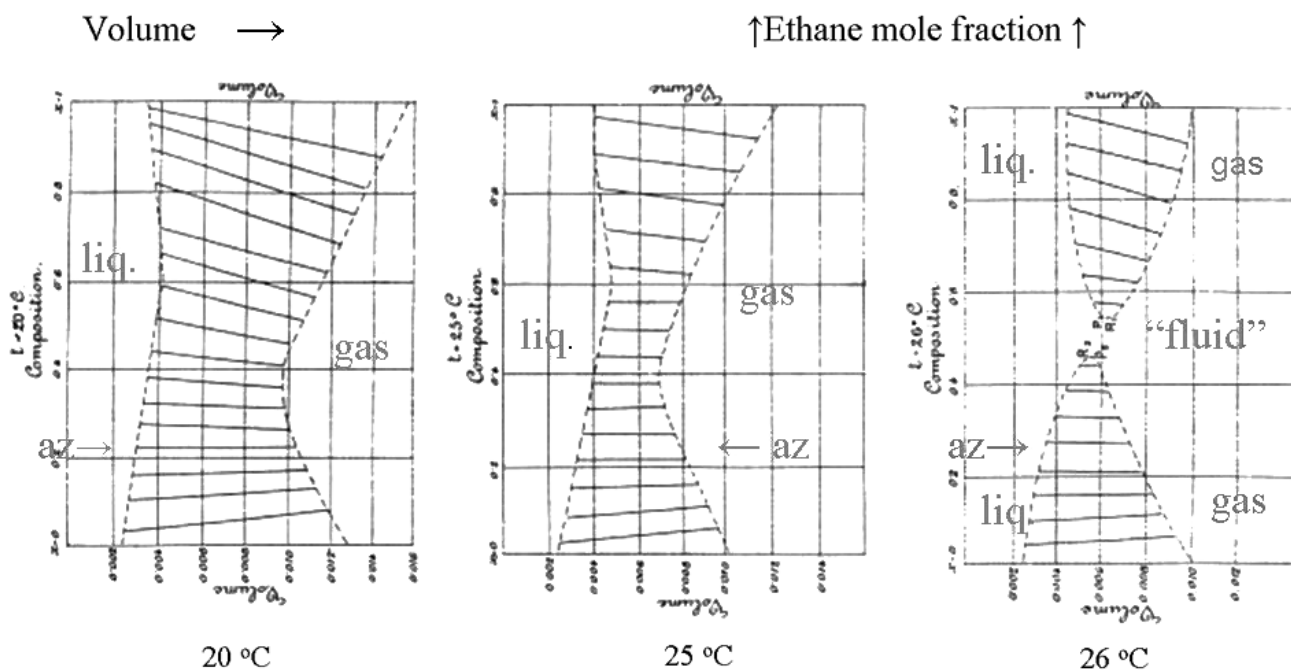


Figure 6. Kuenen’s phase separation experiment [8], in x - V coordinates, in a mixture of N₂O ($x = 0$, bottom) and C₂H₆ ($x = 1$, top), with critical temperatures that are close, but with a minimum in the mixture critical temperature. Left: an isotherm below all mixture critical temperatures shows a transverse fold. The tie-line becomes horizontal at an azeotrope, liquid and vapour having the same concentration. Centre: an isotherm close to the minimum in the mixture critical temperature. A waist develops in the fold, while azeotropy persists. Right: the temperature exceeds the minimum mixture critical temperature, and the transverse fold breaks apart into two folds, each ending in a critical point. The bottom fold displays azeotropy. Reproduced with permission from [5]. Copyright 2002 KNAW.



Figure 7. Group photograph taken outside the Leiden Physics Laboratory in 1909, with Kuenen, second from left, and Keesom, in the rear on the right. The woman next to Kuenen is the daughter of Professor Lorentz. Photograph courtesy of the Leiden Academisch Historisch Museum, reprinted with permission.

(figure 6, left). However, there is a peculiarity in the tie-lines. Although they start tilting away from the horizontal as before, at one mixture concentration there is a *horizontal tie-line*, vapour and liquid having the same concentration, so that they cannot be further separated by distillation—the water–ethanol system is a well known liquid–vapour case. In his mixture paper [3], Van der Waals had studied ‘azeotropy’, as the boiling at constant concentration is called in mangled Greek. Kuenen, however, was the first to detect this phenomenon experimentally near a gas–liquid critical point.

Somewhat closer to the temperature minimum in the critical curve, figure 6, centre, we see the transverse fold developing a waist, while azeotropy persists. Just above the minimum critical temperature, the mixture is above its critical point at certain concentrations, so there is no phase separation for a small range of concentrations in the middle of the diagram; see figure 6, right. Thus, the fold splits in two at a double critical point at the minimum critical temperature, the two partial folds pulling away from each other as the temperature increases. The folds leave the surface at the respective critical points of the pure components. During this entire process, azeotropy persists in one of the folds.

Figure 7 shows a group of Leiden research assistants, including Kuenen and Keesom.

4.4. Connectivity of phase diagrams—Van Laar

The Amsterdam ‘theoretical chemist’ Van Laar (1860–1938), figure 8, had finished his secondary education at a school preparing for service in the Navy (this school was not university preparatory), then studied at the Royal Navy Institute, and spent a couple of years on board ship in the Dutch Navy. He quit, and settled in Amsterdam. Although he was disqualified from obtaining a doctorate, he was allowed to take courses at the university: mathematical physics with Van der Waals, and theoretical chemistry with Van’t Hoff. He



Figure 8. Van Laar, theoretical chemist, University of Amsterdam. The picture was taken around 1906, the time of the experiment discussed here. Photograph courtesy of the Boerhaave Museum, Leiden, reprinted with permission.

venerated Van der Waals, but feelings were not reciprocal. After years of working as a high-school teacher, he tried in vain to obtain a paid lecturer position at the chemistry department of the University of Amsterdam, but found Van der Waals blocking his way repeatedly. For a biography of Van Laar, see [9].

At the time of the 1906 experiment, Van Laar was an unsalaried lecturer in chemistry, and had just completed a series of papers on a realistic version of the VdW equation: the equal-size, geometric-mean equation. Among his achievements was the derivation of an exact expression for the mixture critical loci [10a]. In the process, he made a fundamental discovery. In figure 9, we show his original x – V diagrams, including a number of boundaries of the unstable regions at ascending temperatures, and the loci of critical points indicated by xxx [10b]. In figure 10, we show the bare bones of these complicated diagrams, namely the critical loci as computer generated by Levelt, see [5 chapter 7]. Note that the VdW equation has four special points: the critical points C_1 and C_2 of the components, at $x = 0$ and 1 , respectively, and at $V = 3b$; and two points at close-packing—what he called the ‘third critical temperature’, C_0 , and point A at 0 K. The temperature increases from point A to the critical temperature of the least volatile component C_2 . The left plot shows a continuous vapour–liquid critical curve connecting the critical points of the two components.

The remarkable finding of Van Laar was that if these components have very different critical temperatures, as

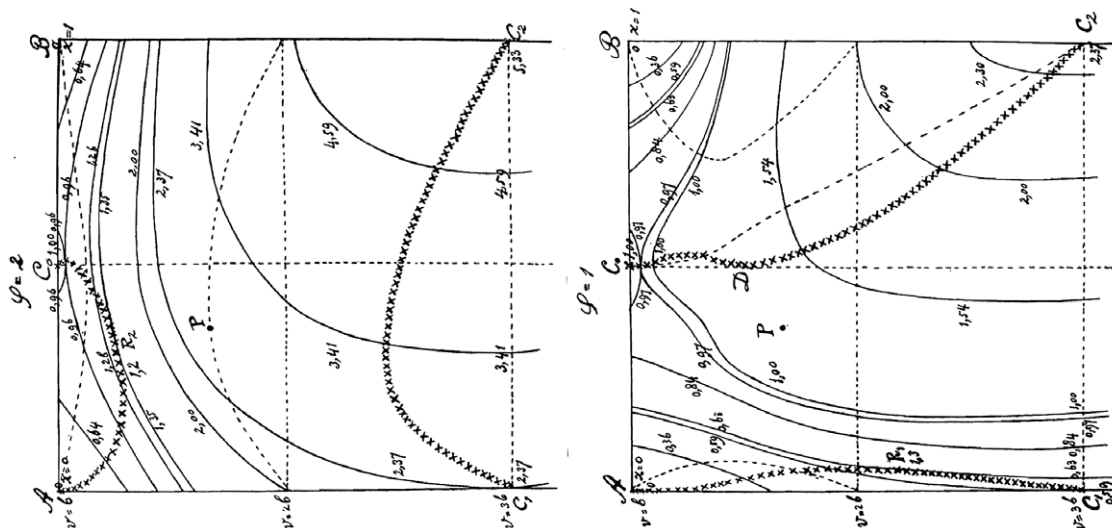


Figure 9. An x - V diagram of boundaries of unstable regions at a number of different temperatures for the geometric-mean VdW mixture according to Van Laar [10b]. In the plot on the right the critical temperatures of the components are much further apart than in that on the left. Loci of critical points are indicated by xxx. For an explanation, see figure 10 and text. Reproduced with permission from [5]. Copyright 2002 KNAW.

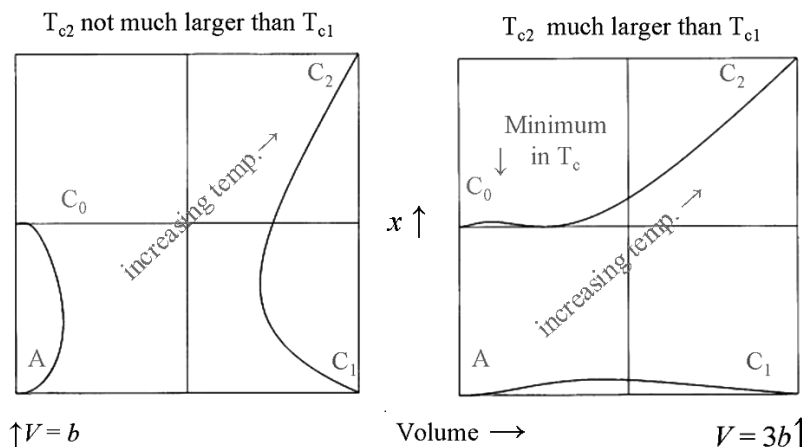


Figure 10. The loci of critical points, computer generated, for the case of figure 9. In the left plot, one critical locus connects the critical points C_1 and C_2 of the components. Another connects the third critical temperature C_0 and the point A at 0 K and close-packing $V = b$. Right: when the critical temperatures of the components are far apart, the connectivity switches and a critical locus runs from C_2 to C_0 . Reproduced with permission from [5]. Copyright 2002 KNAW.

reflected in a large ratio of a_2/a_1 , the vapour-liquid critical curve snaps, and the connectivity of the critical curves becomes that of figure 10, right. The critical point of the less volatile component now connects to the ‘third critical temperature’ C_0 . Van Laar was well aware that Kuenen, now a professor in Scotland, had reported such an interruption of the critical line in the system ethane-ethanol in 1903. For future reference, in this model, the critical locus running from C_0 to C_2 was found to have a shallow temperature minimum near C_0 . Van Laar calculated the coordinates of the point where the connectivity switches. In 1993, Meijer *et al* checked Van Laar’s calculation using symbolic computation and found it to be exact [11]. By the end of 1906, Van Laar had submitted a 50+ page compilation of his results, in French, to the Archives du Musée Teyler [12], while Lorentz and Bakhuis Roozeboom had presented a half dozen of his preceding papers on the topic at

the Academy; these papers were published in the Proceedings in 1905 and 1906.

5. First attempts at understanding barotropy—Van der Waals; Keesom and Kamerlingh Onnes

In what follows, the chronology of events is of importance for an understanding. Therefore, the dates of the Academy presentations have been added in the respective references [1, 13–16]. In the December 1906 session of the Academy Van der Waals, quite intrigued by Kamerlingh Onnes’ November 1906 report on a gas sinking in a liquid [1], made a constructive remark [13]. In the case of azeotropy, the mole fractions of two phases are equal but the molar volumes are different, resulting in the tie-line being parallel to the *volume* axis. If one were to use unit-mass variables

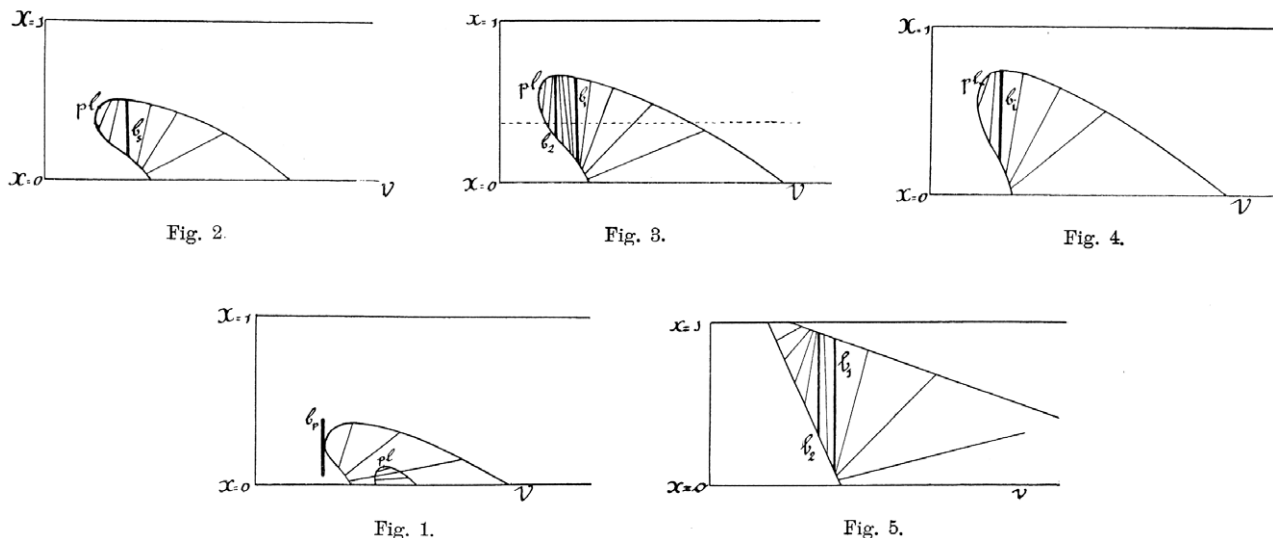


Figure 11. Possible scenarios for the formation of a vertical tie-line needed for barotropy in a diagram where unit-mass coordinates are used. Kamerlingh Onnes and Keesom [15a] still consider a transverse fold in x - V space. Reproduced with permission from [15]. Copyright 1906 Leiden Communications.

for volume and concentration, barotropy occurs when a tie-line runs parallel to the *concentration* axis, since the mole fractions of the two phases are different while the volumes per unit mass are the same. So what was known about azeotropy could be applied to the case of barotropy. Kamerlingh Onnes and Keesom henceforth worked solely with unit-mass variables in their studies of barotropy [14, 15]. Nevertheless, the analogy of the two cases proved less helpful than they hoped for. Keesom [14a] worked out the conditions for a barotropic critical point in liquid–vapour separation, which was presented by Kamerlingh Onnes in the Academy session of 29 December 1906, and he followed up with some numerical estimates of model parameters presented in the 26 January 1907 session [14b]. In the 29 December 1906 session, the two authors [15a] presented inconclusive speculations about the phase diagram, and attempted to find some parameters that would lead to a description of the experiments. In figure 11, we see some scenarios that they had thought up for the phase behaviour of the helium–hydrogen system [15a].

We note that if there were a complete transverse fold (last diagram), the tie-line would have to perform some acrobatics, since it is horizontal at $x = 0$ and 1, but must be vertical in the barotropic point. Although the authors did mention in passing the possibility of a longitudinal fold, they were pretty well fixated on a transverse fold and struggling to make sense of the observed phenomena.

6. Modelling barotropy by the VdW equation—Kamerlingh Onnes and Keesom

Suddenly, in the session of February 1907, the authors presented a novel and plausible model [15b]. The good news was that it allowed the authors to understand the phase diagram. The bad news was that they had to sacrifice the goal

of estimating the helium critical temperature. The model is that of a mixture in which one of the components (helium) has no attraction to itself, or to the second component, but it has an excluded volume that the authors estimated as one-quarter of that of the other component (hydrogen). So the volatile component had no critical point at all. This VdW model was simple enough to do the calculations quickly, and the results are in figure 12.

Note that this is not an isothermal plot: boundaries of the unstable region are indicated for quite a few temperatures $\tau = T/T_c$. The locus of close-packing is now a line of negative slope, since b had been assumed to be linear in x . As soon as the temperature falls below Van der Waals’ ‘critical temperature of complete miscibility’, $\tau = 1.30$, which amply exceeds the hydrogen critical temperature $\tau = 1$, a fold appears on the surface starting at K_m at close-packing. As the temperature decreases, the fold extends further and further into the x - V space. The critical locus comes to an end when the fold reaches the hydrogen critical point at K_1 . At even lower temperatures, the unstable region widens and there will be two coexistent phases over a large part of the phase diagram—this was the situation in the November 1906 experiment, which played out far below the critical temperature of hydrogen. So there is a region of instability leading to phase separation that is vapour–liquid-like at the pure-hydrogen end, and liquid–liquid-like at close-packing. The continuity of states being a fundamental paradigm of Van der Waals, it is disappointing to find pages of discussion on why those two coexisting phases should both be called gas phases [15b].

One further remark is appropriate. It is obvious that in this type of phase diagram, barotropy is unavoidable when the heavy but more volatile component has the smaller molar volume. The tie-line must be horizontal at the pure-hydrogen end, and parallel to the close-packing straight line $V = b(x)$,

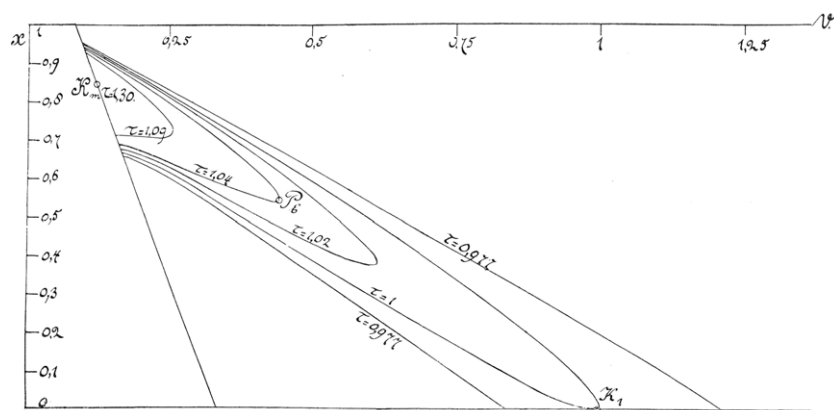


Figure 12. A VdW mixture x - V diagram in unit-mass coordinates, with at $x = 1$, top, a component (helium) without attraction, and therefore without critical point. This component has the smaller close-packed volume, thus the close-packing line $V = b(x)$ has negative slope. Boundaries of the unstable region are shown for a number of values of $\tau = T/T_c$. The critical locus runs from the critical point K_1 of the less volatile component (hydrogen) at $x = 0$ and $\tau = 1$, where it is transverse, to the critical point at close-packing K_m and $\tau = 1$, where it is longitudinal. Reproduced with permission from [15]. Copyright 1906 Leiden Communications.

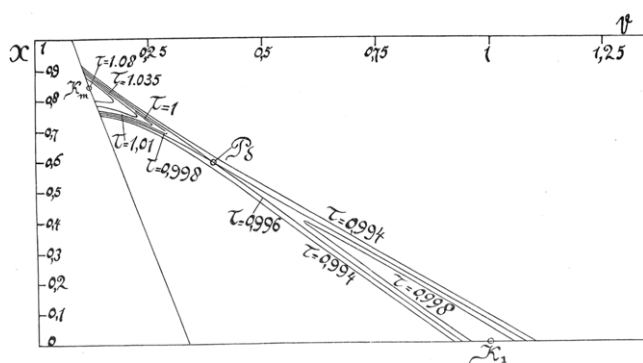


Figure 13. As in figure 12, but with weak attraction for the volatile component (helium) at $x = 1$, whose critical point is not shown. In this case, the locus of critical points has a minimum temperature, with the result that two folds meet in the middle of the diagram, as in figure 6. Reproduced with permission from [15]. Copyright 1906 Leiden Communications.

which has negative slope. The simplest way this can happen is for the tilt to change gradually from the horizontal through the vertical and then to negative slope.

A month later, in an appendix to the February 1907 paper [15b], the two authors introduced a weakly attractive second component, using the geometric-mean rule and thus unwittingly tip-toeing into Van Laar territory. They find that this causes a minimum in the critical temperature, so it is not surprising that figure 13 shows two regions of instability moving into the surface from, respectively, the critical points K_m and K_1 , to meet in a double critical point somewhere in the middle, at a temperature below those of K_m and K_1 , just as in the case of azeotropy (figure 6).

7. The wrath of Van Laar—reaction by Kamerlingh Onnes and Keesom

Van Laar heard or read the 23 February 1907 presentation [15b] and was upset. No wonder—the two authors shrugged off his

work on mixture critical curves as not sufficiently detailed, which is the last thing Van Laar, who documented every single step of each calculation, could be accused of. Realizing that his comprehensive paper for Archives Teyler [12] had not yet appeared in print, he prepared a hasty summary of that paper without having heard or read the 30 March 1907 presentation by Kamerlingh Onnes and Keesom on the case of weak attraction of the second component [15c]. The paper was presented by Professor Lorentz in the meeting of 26 April 1907. First of all, Van Laar judged Kamerlingh Onnes' and Keesom's omission of any criticality of the second component unphysical. Second, he rejected the pages the Leiden authors had devoted to the question of whether the two coexisting phases should be considered gas phases. (Although he was right about that issue, it was a battle he lost: phase separation above the critical temperatures of the two components still goes by the name of gas-gas equilibrium.) Furthermore, he reminded the authors that he not only had discovered the switch in connectivity of the two critical curves, but also had found a temperature minimum on the critical curve that runs to the third critical point K_m . After he read the March 1907 paragraph about the case of weak attraction by Kamerlingh Onnes and Keesom [15c], he must have realized he had been too hasty with his criticism, and penned some additional pages, in which he showed that he had obtained the equation for the minimum in the critical locus in early 1906.

In a quick rebuttal, presented 24 May 1907 [15d] Kamerlingh Onnes and Keesom rejected Van Laar's criticism of the term 'gas-gas equilibrium'. Secondly, they reminded him that it was Van der Waals who had discovered the 'critical temperature of complete mixing', Van Laar's 'third critical point'. Finally, they told Van Laar that he had overlooked the type of phase behaviour without a minimum in the critical curve, which they had found. In a remarkably meek reply [16b], Van Laar conceded this last point, but insisted that he was the one who first published the model of Kamerlingh Onnes and Keesom's March 1907 paper with the temperature minimum in the critical locus.

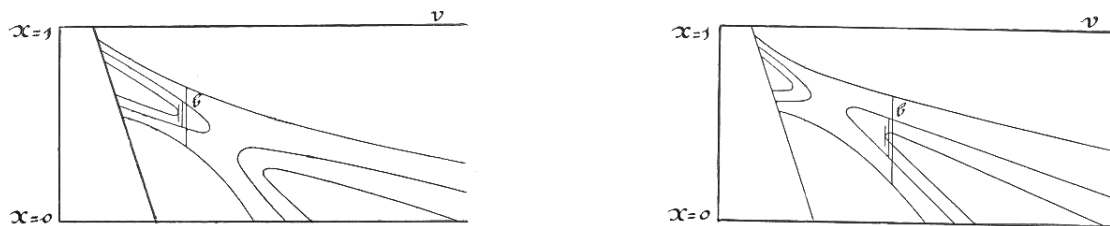


Figure 14. Kamerlingh Onnes and Keesom have fully understood phase separation and barotropy in a model for the hydrogen–helium system [15d]. An x – v diagram in unit-mass coordinates, as in figures 12 and 13. The vertical tie-lines indicate examples of the occurrence of barotropy at various temperatures. Reproduced with permission from [15]. Copyright 1906 Leiden Communications.

All is well that ends well. In their last paper in the series [15e], presented 27 October 1907, which displays a complete understanding of barotropy, see figure 14, Kamerlingh Onnes and Keesom scrupulously refer to all of Van Laar’s relevant work.

8. Conclusion

A brief burst of scientific research, towards the end of the long path to helium liquefaction in Leiden, illustrates the scientific curiosity of Kamerlingh Onnes, the advanced experimental facilities Leiden researchers had available, and the store of knowledge and experience about fluid mixture behaviour accumulated by the Dutch School. Almost all members of this school contributed, directly or indirectly, to elucidating the barotropic effect in helium–hydrogen mixtures.

At the end of their first joint paper [15a], Kamerlingh Onnes and Keesom raised the interesting question of how the phases would arrange themselves if hydrogen were to solidify. Eighty years later, Schouten and Van den Bergh [17] studied helium–hydrogen mixtures pressurized in a diamond anvil cell the size of the head of a pin. In a mixture with 20% mole fraction of helium, they observed at 5.7 GPa and 280 K a complete inversion of the three phases, the solid phase floating on top.

Unfortunately, the original goal of the Leiden researchers, obtaining an estimate of the critical temperature of helium, was not reached. So the Leiden staff continued the tedious work of measuring hydrogen and helium PVT data down to cryogenic temperatures. By the end of 1907, sufficient data had been obtained to produce an estimate of 5.2 K for the helium critical temperature, which turned out to be within 0.01 K from the current best value of 5.19 K. Although he did caution about possible departures from the law of corresponding states for these two cryogenic fluids, Kamerlingh Onnes was now convinced that liquefaction was feasible. In the middle of the following year, he and his staff produced the first liquid helium.

Acknowledgments

The author is grateful to her NIST, Boulder, colleagues Arno Laesecke, Allan Harvey and Ray Radebaugh, for their help, advice and constructive criticism. She thanks her brother

Antonius Levelt, who computer-generated figure 10, and Ellie Rijsewijk, who scanned several of the original graphs. She is very grateful to Professor Peter Kes for inviting her to speak during the LT25 historic excursion to Leiden, and for his generous help in getting the figures and manuscript ready for publication.

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