

## II. Dilute near-critical mixtures – Van 't Hoff, Van der Waals, Korteweg, Verschaffelt, Keesom, and Van Laar

### II.1 *Introduction*

In this last chapter on topics studied by the school of Van der Waals and Kamerlingh Onnes, almost all members encountered earlier gather around a common interest: the behavior of dilute mixtures near critical points. Why was this? One reason was that the universal laws for the thermodynamic behavior of dilute solutions had moved to the center of attention at that time. What happens to these laws near the solvent's critical point was a natural and compelling question for the Dutch School, which was uniquely equipped to address it. Another motivation was the need to quantify the effect of impurities in experiments near critical points, as discussed in the previous chapter. It became urgent to model impurity effects. In the process, it was found out that the effect of impurity on the fluid density is exceptionally large near the solvent critical point.

This chapter begins with the behavior of dilute mixtures away from criticality. Near infinite dilution, such mixtures have very special and interesting characteristics elucidated in the 19<sup>th</sup> century, with major contributions by Jacobus Henricus Van 't Hoff, a chemistry professor at the University of Amsterdam from 1877 to 1896. He won the first Nobel prize in chemistry, the centennial of which was celebrated in 2001. It seems fitting to pay tribute to Van 't Hoff in this chapter, even though his interactions with Van der Waals were minimal.

The emphasis of the chapter then shifts to the behavior of dilute solutions near critical points. After an introduction from the modern perspective, contributions by Van der Waals, Korteweg, Verschaffelt, Keesom and Van Laar will pass review. Each of them approaches the problem in a way reflecting his special expertise and interest. The chapter closes with remarks regarding the revival of interest in dilute near-critical mixtures triggered by a topic widely studied in the last part of the 20<sup>th</sup> century, that of supercritical fluids as solvents.

## 11.2 *Van 't Hoff and mixtures near infinite dilution*

11.2.1 *Biographical.* E. Cohen (1912), a former pupil, colleague and friend of Van 't Hoff, published an extensive biography (in German) the year after the latter's death. Recently, Cordfunke (2001) published (in Dutch) a succinct overview of Van 't Hoff's life and the significance of his work. These sources have provided the following facts. Jacobus Henricus (Henry) Van 't Hoff (1852-1911) originated from an upper-middle-class family, his father being a physician in Rotterdam. The family had a comfortable existence, but since he and three younger brothers would all receive a university education, finances were sometimes tight. A precocious and brilliant student in high school, he studied calculus and technology at the Delft Polytechnic, and physics with Professor Rijke in Leiden in 1871 and 1872. He took classes along with Lorentz and Van der Waals, the latter being 15 years his senior. After his 1872 candidaats exam (roughly equivalent to a bachelor's degree), he studied abroad for a while, which was not customary for beginning graduate students in those days. He spent the academic year 1872/73 in Bonn, Germany, with the chemist August Kekulé, famous for his proposition of the ring structure of benzene. He then returned to the Netherlands and obtained his doctoral exam (roughly equivalent to a Ph.D. qualifying exam) at the University of Utrecht in December, 1873. Then he spent another six months in France, where Adolph Wurtz and Joseph Achile Le Bel at the faculty of medicine in Paris strengthened his interest in structural organic chemistry. By the summer of 1874, Van 't Hoff returned to the Netherlands, applying in vain for a HBS teaching position. He felt fortunate when he acquired a teaching position at the Veterinary School in Utrecht, where he found he had plenty of time to spend in the laboratory.

In the fall of 1874, at the age of 22, Van 't Hoff proposed, in an 11-page Dutch manuscript, the hypothesis that forms the foundation of organic chemistry and the life sciences: the tetrahedral arrangement of the bonds of the carbon atom. He did this on the basis of the known number of isomers of substances containing an 'asymmetric' carbon atom, one that was bonded to four different atoms or groups. If the bonds were in a plane, there should be three different isomers, and no mirror images. In a tetrahedral arrangement in space, however, there should be only two isomers, and these two would be optically active mirror images of each other. It was known that the latter was the case. This proof was brilliant, but its force escaped some of the learned professors that reacted to his paper. Although the hypothesis intrigued them, they advised Van 't Hoff to go back to the laboratory and find out experimentally whether his hypothesis was really true, see Cohen (1912).



Jacobus Henricus van 't Hoff.  
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The tetrahedral model raised the level of reality of molecules, just at the time that thermodynamics experts such as Ostwald and Mach considered molecular existence unproven, and the molecular hypothesis unnecessary. Before Van 't Hoff's hypothesis, a chemical formula such as  $\text{H}_2\text{O}$  could still be interpreted in minimalist way, as representing a reaction of two volumes of hydrogen with one volume of oxygen, forming a new compound. The young Van 't Hoff, however, had the vision to ascribe a spatial arrangement to the bonds of a molecule, and proved its validity.

Van 't Hoff had a meteoric career. When the Amsterdam Athenaeum was converted to a university in 1877, he was appointed a lector of chemistry, and in 1878 he received a professorship, becoming a colleague of the much older Van der Waals. He was elected to the Royal Netherlands Academy of Arts and Sciences (KNAW) in 1885, and to the Holland Society of Sciences and Humanities (HMW) in 1890. His talent was widely recognized and appreciated both in

Holland and in Germany. Repeatedly, he received offers for prestigious positions abroad. In particular, he used an offer from Leipzig University in 1887 to obtain a new chemistry building at the University of Amsterdam, which cost the city an exorbitant amount of money. (As a student, the author of this book took some of her chemistry classes in this cavernous building, but it burned down in 1987.) In 1896, however, Van 't Hoff accepted an offer from the Prussian Academy of Sciences in Berlin, as the teaching load in Amsterdam was too much for him. In 1901 he received the first Nobel prize in chemistry. Surprisingly, it was not given for the asymmetric carbon atom, although this work was highlighted in the laudatory speech by Dr. Odhner, President of the Royal Swedish Academy of Sciences, but for Van 't Hoff's work on the chemical thermodynamics of dilute solutions. Van 't Hoff indeed laid the thermodynamic foundation for the physical chemistry of solutions and for reaction chemistry, by equations that carry his name and that are used by chemists to the present day.

Although the tenures of Van der Waals and Van 't Hoff at the University of Amsterdam overlapped for 20 years, they did not collaborate. Nevertheless, Van 't Hoff immediately grasped the importance of Van der Waals's work on mixtures for extending osmotic theory to higher concentrations. As a co-editor, with Ostwald, of the *Zeitschrift für Physikalische Chemie*, he arranged for translation into German and rapid publication of Van der Waals's (1890) paper on mixtures before the original French version of 1891 went to press, see Kipnis *et al.*, (1996) 114-115. Van der Waals's profound influence on the Amsterdam chemists came to the fore only after Van 't Hoff left for Berlin, to be succeeded by Bakhuis Roozeboom in 1897.

Van 't Hoff received the Nobel prize in 1901, at the age of 49. Van der Waals would have to wait for another decade, and was in his seventies when he was finally so rewarded.

11.2.2 *What is magic about dilute solutions?* In order to explain the importance of Van 't Hoff's work, we make an analogy with ideal-gas law,  $PV = RT$ . This law is universal, since it contains no particulars of the gases it applies to. No actual gas, however, obeys the law exactly. At low density, there are usually small positive or negative departures between  $PV$  and  $RT$ . Near a critical point, however, the departures are huge, and condensation cannot be described at all. Nevertheless, the law is of utter importance in theory and in practice. It serves as an anchor point in the limit of zero density (infinite molar volume). Any theoretical equation of state needs to be thus anchored. Experimental data that appear to miss this limit are thereby suspect.

Ch. 4.1 introduced Dalton's generalization of the ideal-gas law to mixtures,  $P = \sum P_i = \sum n_i RT$ , Eq. (4.1). Each component  $i$  is assumed to exert a partial

pressure  $P_i$  independent of the others, given by Boyle's law and therefore proportional to the mole number  $n_i$  of component  $i$ . The total pressure equals the sum of the partial pressures. Again, this low-density limiting behavior serves as an anchor point for the description of the behavior of gas mixtures.

The ideal-gas laws are valid to the extent that the interactions between the molecules of the gas can be neglected, that is, at low density. The focus of the school of Van der Waals, however, was on departures from the ideal-gas law caused by the molecular interactions.

One may characterize Van 't Hoff's work as the development of a set of anchors for solutions, analogous to the ideal-gas law. A solution is a special type of mixture in which one component, the solvent, is a liquid usually well below its boiling point, with low compressibility and a vapor pressure far below an atmosphere. The other component, the solute, may be solid, liquid or gas, and is usually assumed to be present in relatively small amounts. In such a case, the interactions between solute molecules can be ignored, but interactions between molecules of the solvent, or between solvent and solute, are strong and ever present. Nevertheless, at low solute concentration, the solution becomes ideal, and the properties of the solution and the characteristics of chemical reactions between solute molecules assume a simple and universal concentration dependence. Chemistry owes this profound insight in large measure to Van 't Hoff.

As early as the 1880s it was quite well known that adding a volatile solute to a solvent, such as water, lowers the vapor pressure and therefore lowers the freezing point and increases the boiling point. On the basis of his experiments, Raoult, in 1887, proved that for low concentrations those effects are proportional to the mole fraction of the solute, but entirely independent of its nature. (For dissociating solutes, it is not the number of moles, but the number of independent entities that counts.) These universal dilute-mixture effects are called *colligative* properties. Eq. (4.2),  $(P_0 - P) / P_0 = x_i$ , for the lowering of the vapor pressure of a solution due to an admixture, is an example of a colligative property.

The colligative property studied by Van 't Hoff was osmosis, an effect known from the 18<sup>th</sup> century. If a solution, such as sugar in water, is covered by a layer of pure water, the sugar will slowly spread through the water until the concentration is the same throughout. If a sturdy membrane is put between the sugar solution and the water such that water can pass through, but sugar cannot, water is driven to the side of the solution, and pressure builds up in the solution until it stops further transport of water to the solution. Van 't Hoff called this measurable pressure buildup through a semi-permeable membrane the *osmotic pressure*  $\Pi$ . Van 't Hoff, as well as other chemists in the late 19<sup>th</sup> century, measured the osmotic pressure as a function

of concentration and found that, for low concentrations, it was proportional to the concentration and independent of the nature of the solute. Careful measurement established, moreover, that the osmotic pressure equals.

$$\Pi = c RT; \quad c = n_2/V \quad (\text{II.1})$$

with  $V$  the volume of the solution,  $n_2$  the moles of solute, and  $c$  the concentration of solute. Van 't Hoff derived this law in 1885. He pointed out its implication: the osmotic pressure equals the pressure that an ideal gas would exert in the cell if would contain as many moles per unit volume as the solute in the solution, independent of the character of the solute.

Van 't Hoff put the laws governing colligative properties on a thermodynamic basis by imagining appropriate thermodynamic cycles, while making use of semi-permeable membranes to move components in and out reversibly. In his design of such cycles, he always used the ideal-gas law for vapor phases, and assumed a state of high dilution in the solution. He invented his proofs afresh, avoiding the use of Gibbsian thermodynamics and the phase rule. His most important work was in the field of chemical reactions. He postulated by intuition, see Cordfunke (2001), the famous relations for the change of the chemical equilibrium constant with temperature and pressure in terms of the standard-state heat and volume of reaction. These relations were proved to be exact, and they form the foundation of chemical thermodynamics. In solution chemistry, a commonly used standard state from which to measure departures from ideality is that at infinite dilution of the reacting solutes.

**II.2.3 Critique.** The laws derived by Van 't Hoff for the osmotic pressure, Eq. (II.1), as well as for other colligative properties, were defined in terms of concentration dependence, and were strictly valid only in the limit of infinite dilution. Van 't Hoff was well aware of this, but many of his followers were not. As clearly stated by Gibbs (1876, 1878), the key is in the chemical potential of the solvent, which must be equal on both sides of the membrane. If interactions between solute molecules can be neglected, the most important concentration-dependent contribution to the chemical potential of the solvent comes from the Gibbs mixing term, which for small concentration assumes the simple universal form of  $-RTn_2/n_1$ ; here  $n_1$  equals the moles of solvent in the volume  $V$ . In addition, the (small) increment of pressure,  $\Pi$ , on the side of the solution contributes  $(V/n_1)\Pi$  to the solvent chemical potential. Setting the sum of these contributions to zero keeps the chemical potential of the solvent in the solution equal to that of the pure solvent on the other side of the membrane and results in Eq. (II.1). For small  $\Pi$ , the pressure buildup must therefore be proportional to  $c$ , independent of the nature of the solute.

It is understandable that enthusiastic followers immediately began to apply this law at any concentration. Worse, Van 't Hoff's observation that the osmotic pressure happens to equal the pressure that the solute molecules would exert if they would be moving freely in the volume occupied by the solvent, was widely interpreted by German chemists as a physical explanation of the origin of osmotic pressure. These developments drove the Amsterdam chemist Van Laar to a high pitch of strident indignation. For the rest of his life, he conducted a one-man crusade against the concept of osmotic pressure, and against the German 'Osmotic School,' see Snelders (1984). He did not mellow with age. In 1915, he attacked Ehrenfest, who had had the temerity to write an article on the kinetic interpretation of osmotic pressure. To Van Laar, the driver of osmotic effects is the difference in chemical potential of the pure water and the water in the solution. The story of sugar molecules, unencumbered by the solvent, flying around in the cell and impinging on membranes, was anathema to him.

Van Laar, of course, justly criticized this interpretation. A sound basis for describing both the colligative effects and the corrections needed for systems not at infinite dilution could only be found by systematically applying Gibbsian thermodynamics. Curiously, the only references to Van der Waals in Cohen's (1912) voluminous biography are exactly about this point. Van 't Hoff, while careful about the fact that the laws proposed by him are valid only in the limit of infinite dilution, repeatedly refers to Van der Waals as the one who would know how to proceed away from this limit. From this perspective, the present chapter makes the point that 'moving away' from the infinite – dilution limit is very different if the solvent is at its critical point, rather than in an incompressible liquid state.

Van 't Hoff, who shunned the complex mathematical machinery being put into place by Van der Waals and who did not appreciate Bakhuis Roozeboom's phase theory, was able to obtain the fundamental limiting laws of chemical thermodynamics by simple means and sound intuition. These laws bear his name, and, properly generalized, find application to this very day. The Nobel prize was well deserved, even if not given for the asymmetric carbon atom.

### 11.3 *A solute added to a solvent at its critical point*

In this section, we introduce from a present-day perspective the concepts and properties that will be encountered in the historic narrative to follow. For details, reviews and references, see Levelt Sengers (1991, 1993).

11.3.1 *Solute-induced phase separation.* Near infinite dilution, adding a solute to a solvent results in changes in the solvent properties that are proportional to the amount of solute and of a universal nature. This is not always so if the

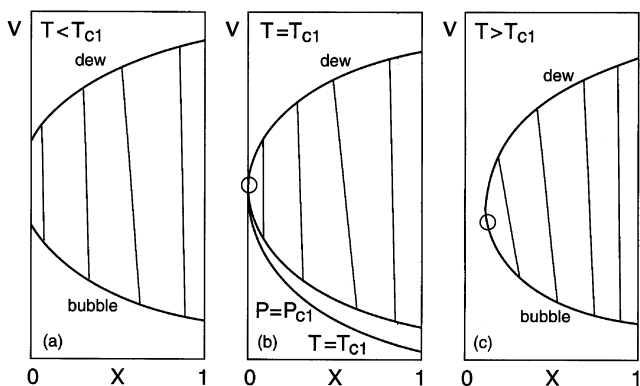


Fig. 11.1 The plait and its tie lines for a low-volatility solute, in the  $V$ - $x$  diagram, for a temperature just below (a), at (b), or above (c) the solvent critical point. The isothermal connodal (coexistence curve, or dew-bubble curve) is shown. The tie lines slant, but become vertical at  $x = 0$  and  $x = 1$ . In (b), not only the connodal, but also the curve of constant pressure ( $P = P_{c1}$ ,  $T = T_{c1}$ ) has been shown. The circles indicate the solvent critical point (b), or the plait point (c).

solvent is at its critical point. One reason is that the solute may induce a phase transition, which is a catastrophic effect rather than a smooth change proportional to the amount of impurity.

To explain why this is so, we draw in Fig. 11.1 isothermal  $V$ - $x$  plots, with  $V$  the molar volume, and  $x$  the mole fraction of the solute. These plots are shown for the cases that the principal component, the solvent, is just below (a), just at (b), or just above (c) its critical temperature, while the solute, far less volatile, is way below its critical point. The feature at  $x = 0$  is the one to watch first. In case (a), the solvent is just below its critical temperature, so at  $x = 0$  there are coexisting liquid and vapor phases that have almost, but not quite, the same molar volume. In case (b), the critical temperature, these two volumes have just become equal. In case (c), the solvent is above its critical point, and there is no longer vapor-liquid coexistence at  $x = 0$ . The behavior on the  $x = 1$  axis, however, is entirely unremarkable. The solute is way below its critical point, and therefore a small-molar-volume liquid and a high-molar-volume vapor are coexisting at all three temperatures.

We now pay attention to the plait on the surface. In case (a), the transverse plait simply runs across the entire diagram. This is not necessarily so: azeotropy, or the occurrence of an additional fluid or solid phase, may interrupt the plait (Fig. 6.6). We assume the absence of such interruptions here, so as not to complicate the argument. In case (b), the plait comes in from the

right, and just closes at the pure-solvent critical point on the  $x = 0$  axis. In case (c), the plait comes in from the right and closes at a critical point before it reaches the  $x = 0$  axis.

To find the critical point of the mixture, we pay attention to the tie lines. Since the solute is of low volatility, we expect it to shun the vapor and concentrate in the liquid. Thus, the tie lines should slant from top left to bottom right. There is an exception: at  $x = 0$  and at  $x = 1$ , the tie lines must be vertical, because only one of the components is present and its mole fraction is unity in both phases. This leads to the tie lines shown schematically in Figs 11.1. The mixture critical point in Fig. 11.1c is the point where the tie line shrinks to zero, and we would not be surprised to find it slightly off to lower volumes in this particular case of an involatile solute and an uncomplicated plait.

Thus by adding an involatile solute to a slightly supercritical solvent, a two-phase region is entered. This is a disruptive event instead of a smooth change proportional to the amount of impurity.

11.3.2 *What happens to the plait point?* As the impurity is added, the plait point shifts in general to a slightly different temperature  $T_{pl}$  and pressure  $P_{pl}$ . In the particular example of a nonvolatile solute, Fig. 11.1c, for instance, we notice that the plait point temperature must be above that of the solvent, but in practice a downward shift is just as common. We will see that both the Amsterdam and Leiden scientists invested ingenuity and effort in calculations of the derivatives  $dT_{pl}/dx$  and  $dP_{pl}/dx$ . They found that the shift of the plait point temperature and pressure is linear in  $x$  for small  $x$ , but most certainly not universal. In the process, they found a number of interesting relations between these shifts and a variety of derivatives of the Helmholtz energy or the pressure evaluated at the solvent critical point.

11.3.3 *The shape of the isothermal coexistence curve.* The most interesting case is that when the solvent is at its critical point, Fig. 11.1b. First of all, near  $x = 0$ , the coexisting phases still have different molar volumes, but they have almost the same mole fraction. For mean-field equations of state, the conodal (coexistence curve) is a parabola tangent to the volume axis. At the solvent critical point, therefore, the roles of  $V$  and  $x$  are distinctly different. A small amount of solute added at the solvent critical temperature leads to a split into two phases of considerably different density. For instance, at the solvent critical point, a 1%-level addition of impurity leads to two phases with a density difference of the order of 10%.

11.3.4 *The shape of the critical isotherm-isobar.* The Leiden researchers were most interested in the question of the difference in density between a pure

fluid at its critical point, and that of a dilute mixture at the same pressure  $P_c$  and temperature  $T_c$ . The answer will reveal what density differences can persist due to un-equilibrated impurities in a fluid at its critical point.

For a nonvolatile solute, the isotherm-isobar at the solvent critical point must run in the liquid phase, as shown in Fig. 11.1b. For a mean-field equation of state it is part of a cubic, with a vertical tangent at the solvent critical point. Mathematically, this can be expressed in the following way:

$$\text{At } P = P_c, T = T_c, \text{ near } x = 0: (V - V_c)^3 \approx x \quad (\text{II.2})$$

This implies that the derivative  $(\partial V/\partial x)_{P,T}$  becomes infinite at the solvent critical point. This derivative serves to define the partial molar volumes of solvent and solute,  $V_1$  and  $V_2$ , given by

$$\begin{aligned} V_1 &= V - x (\partial V/\partial x)_{P,T} \\ V_2 &= V + (1-x) (\partial V/\partial x)_{P,T} \end{aligned} \quad (\text{II.3})$$

Here  $V$  is the molar volume of the solution.

The partial molar volumes, as a characteristics of solvent and solute, were used by Bakhuis Roozeboom, but not by Van der Waals and Kamerlingh Onnes. The partial molar volume is one of many similarly defined partial molar properties introduced early in the 20<sup>th</sup> century for characterizing mixture behavior, and presently universally used. See, for instance, Rowlinson and Swinton (1982). In dilute mixtures, partial molar properties usually have very simple behavior, the partial molar properties of the solvent approaching those of the pure solvent, and those of the solute approaching a finite limit. At the solvent critical point, however, this simple behavior no longer prevails. It is clear from Fig. 11.1b, for instance, that when  $x$  approaches 0 at the solvent critical point, the partial molar volume of the solute,  $V_2$ , becomes infinite. The same conclusion follows from the mathematical identity

$$(\partial V/\partial x)_{P,T} = - (\partial P/\partial x)_{V,T} (\partial V/\partial P)_{x,T} = (\partial P/\partial x)_{V,T} (V K_T) \quad (\text{II.4})$$

Since  $(\partial P/\partial x)_{V,T}$  is finite and non-zero, it follows that in the limit of infinite dilution the partial molar volume of the solute diverges just like the compressibility  $K_T$  of the pure solvent. The sign and strength of the divergence are determined by the derivative  $(\partial P/\partial x)_{V,T}$ , see Ch. 11.3.5.

The fact that the isotherm-isobar is a cubic with vertical tangent is the reason that near the solvent critical point a small impurity causes a disproportionately large density change, which is not linear in the concentration. It implies that, at the critical pressure and temperature of the pure host, a 1 part in 1000 impurity causes a density increase of the order of 10%! This is a huge effect, quite contrary to the usual linear departure

from infinite dilution. It easily explains the strange phenomena observed in so many laboratories where sample purity was not a high priority (Ch. 10). The Leiden researcher Verschaffelt found a way of estimating the size of this effect in the early 1900s.

At the solvent critical point, therefore, the simple rules for colligative properties, that effects are proportional to concentration, must fail. Rightly, Van 't Hoff pointed to Van der Waals holding the key to formulation of the thermodynamic behavior of mixtures not infinitely dilute, and with vapor phases that are not ideal.

11.3.5 *Some other useful derivatives.* The critical-point value of the derivative  $(\partial P/\partial x)_{V,T}$ , introduced in Eq. (11.4), is a well defined, finite, generally non-zero, non-universal quantity in mean-field theory. It reveals how much the pressure falls or rises if in a fluid at its critical point, kept at constant volume, a small number of solvent molecules are exchanged for solute molecules. If the solute is highly volatile, such as hydrogen in carbon dioxide at its critical point, an increase in pressure is to be expected and the derivative  $(\partial P/\partial x)_{VT}$  is positive. A low-volatile solute, such as a salt in near-critical water, will lead to a decrease in pressure, so that the derivative is negative.

When a solute is added to a solvent at its critical point, a mixture critical line develops starting at  $x = 0$ . In Fig. 11.2 we show this situation in a  $P$ - $T$  diagram. There are two important slopes in this picture: that of the vapor pressure curve,  $(dP/dT)_\sigma$ , of the pure solvent at its critical point, and that of the incipient critical line,  $dP_{pl}/dT_{pl}$ . As to the first one, Van der Waals (1905b) showed that for pure fluids,  $(dP/dT)_\sigma$  equals the slope of the critical isochore,  $(dP/dT)_V$ . See Ch. 11.4.5 and 11.4.8. This means that in Fig. 11.2, the pressure-temperature relation for the one-component fluid at its critical density does not change slope when the fluid passes through its critical

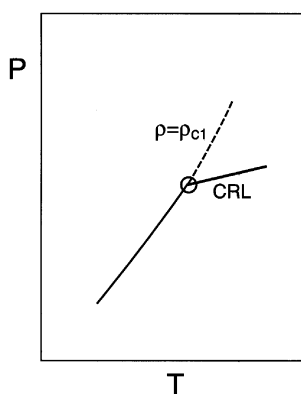


Fig. 11.2 In the  $P$ - $T$  diagram, the vapor pressure curve and the critical isochore  $\rho = \rho_{c1}$  of the pure solvent, (1), are shown, along with the beginning of the critical line, CRL. The circle indicates the solvent critical point.

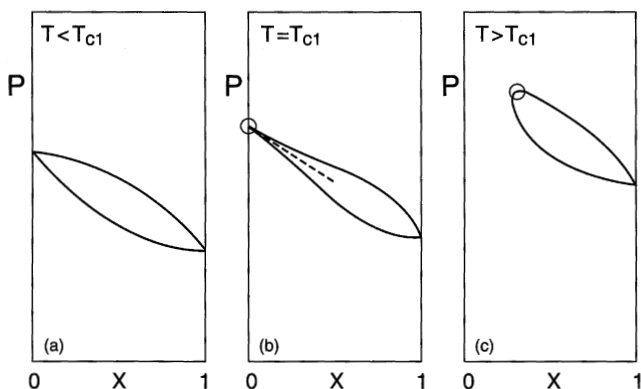


Fig. 11.3 Near-critical isothermal dew-bubble curves in the  $P$ - $x$  diagram, for a solute of low volatility. The behavior is shown (a) just below, (b) at, and (c) above the critical temperature of the solvent. The circle indicates the solvent critical point (b), or the plait point (c). At the critical point, the dew-bubble curve narrows to a 'bird beak.'

point. The derivatives  $dP_{pl}/dT_{pl}$ ,  $dT_{pl}/dx$  and  $dP_{pl}/dx$  obey a simple thermodynamic relationship, see Ch. 11.4.5.

11.3.6 *The shape of the mixture dew-bubble curve in the  $P$ - $x$  plane.* In Fig. 11.3, we draw attention to a peculiarity of the dew-bubble curve in the vicinity of the solvent critical point for the case of a solute of low volatility. Just below the solvent critical point, case (a), the dew-bubble curve has the normal appearance, with a finite angle between the two branches. Above the solvent critical point, case (c), the dew-bubble curve does not reach the  $x = 0$  axis any more. At the critical point, case (b), the two branches have a common tangent with, in general, finite non-zero slope. Van der Waals (1905b) proved this 'bird-beak' feature. It was rediscovered by Wheeler (1972), see Ch. 11.5.

#### 11.4 *The Dutch school and dilute near-critical mixtures*

11.4.1 *Overview.* Van der Waals (1895a,b) derived, as exact thermodynamic relationships, the first limiting laws for the shift of the critical pressure with temperature due to an admixture. The first experiments and modeling of impurity effects began in Leiden shortly before the turn of the century. Verschaffelt and Keesom were principal players. The experimental data they used for tests were those Verschaffelt had obtained around 1900 for the system carbon dioxide with small fractions of hydrogen. For the modeling, they used

various forms of the law of corresponding states, in keeping with the Leiden tradition of preferring this law over the Van der Waals equation.

Around 1900, the mathematician Korteweg, who had been silent on the matter of fluid mixtures for a decade, took an interest in the problem of impurity effects near criticality. He produced a calculation of impurity effects in the  $V$ - $x$  diagram on the basis of the Van der Waals equation for mixtures, in his own systematic fashion. Korteweg (1903) published this work in French and in English. A large color graph is part of his paper.

At roughly the same time, Keesom and Verschaffelt independently began deriving expressions for the initial slopes of the plait point curve. This effort stranded because of the impossibility to obtain from experiment with any degree of reliability the second derivatives occurring in their various expressions. Verschaffelt (1906a) then turned around and, quickly and effectively, developed a reliable method for estimating impurity effects, based on the superposition of nets of experimental  $P$ - $V$  isotherms for the pure solvent and a dilute mixture of constant composition. Van Laar (1905e,h) derived simple expressions for the shift of the plait point temperature with concentration for his specialty: the van der Waals geometric-mean mixture model. Van der Waals (1905a,b) reminded all parties involved that he had worked on this problem ten years ago, but he did use the opportunity to publish a number of proofs of interesting and relevant identities that had been lying in his desk drawer for a long time.

After briefly reviewing Van der Waals's (1895) papers, we will first discuss Korteweg's (1903) pictures, the results of Keesom (1901) and Verschaffelt (1902a, 1902b, 1903, 1906a,b), and finally, the work of Van Laar (1905e,h) and Van der Waals (1905a,b).

11.4.2 *Van der Waals and the slope of the critical line.* Van der Waals's (1895a,b) papers give an exact expression for the derivative  $dP_{pl}/dT_{pl}$  for any concentration along the plait point curve in terms of second derivatives of both the energy and the Helmholtz energy. Also, Van der Waals gives the analogous result for the limit of infinite dilution. With no direct link to experiment, Van der Waals's relations, although exact, were not particularly useful. Keesom (1901) rewrote these equations for dilute mixtures, replacing the energy and Helmholtz energy derivatives by the more convenient derivatives of the pressure, to be discussed in Ch. 11.4.5. This is the reason we do not give Van der Waals's expression here.

11.4.3 *Korteweg's mathematical analysis of the Van der Waals model near the solvent plait point.* A picture is the centerpiece of the Korteweg (1903) paper. Fig. 11.4 shows the top part of the large-scale graph in the back of his paper.

There are eight possible locations of the dilute-mixture plait point with respect to the pure-fluid critical point. One such case was introduced in Ch.11.3.1 and was shown in Fig 11.1. Korteweg considers all possible cases for the Van der Waals model for mixtures.

Korteweg displays the condition of a dilute mixture, kept at a constant temperature close to but not equal to the critical temperature of the solvent, in an isothermal  $V$ - $x$  plane. The point  $K$  indicates the critical volume of the pure solvent, while  $P$  indicates the plait point volume and concentration.  $K$ - $P$  is the projection onto the  $V$ - $x$  plane of the initial part of the critical line, which itself is, of course, not isothermal. The full curve is the isothermal connodal or coexistence curve, ending in  $P$ , and the dashed curve is the isothermal spinodal through  $P$ . The point  $R$  is the largest concentration reached on the connodal. Its location with respect to  $P$  determines the nature of the retrograde behavior (Ch. 6.6).

Considering the four pictures in the left column, we note that they represent situations as in Fig. 11.1c, where the temperature is slightly *higher* than the critical temperature of the solvent: the plait does not intersect the  $V$  axis, and thus there are no solvent coexisting phases present. The solute is far *below* its critical point, and much less volatile than the solvent. As the temperature decreases, the plait will touch the  $x = 0$  axis at the solvent critical temperature. Below this temperature, the plait point disappears and the plait runs over the full length. On the left, Korteweg has collected all possible arrangements of  $K$ ,  $P$  and  $R$  for this case.

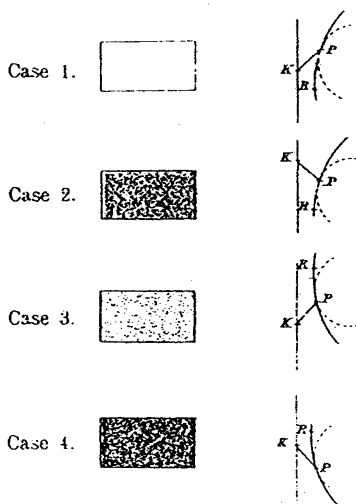
Considering now the four isothermal pictures on the right, we note that the temperature is below the critical point of the solvent. The plait intersects the  $V$ -axis at  $x = 0$  in two points, which represent a low-volume liquid phase and a high-volume vapor phase, with the critical volume somewhere in the middle. The plait disappears at  $P$ , the plait point, and, if it does not reappear as  $x$  increases, it will not reach the  $x = 1$  axis (the case of azeotropy is an example of reappearance of the plait). The solute is *above* its critical temperature, and thus in general more volatile than the solvent. As the temperature drops towards the critical point of the solvent, the plait point  $P$  moves towards  $K$ . Below the solvent critical temperature, there is no plait on the surface.

A further division of Korteweg's eight cases is based on the location of the plait point  $P$  with respect to the solvent critical point  $K$ .  $P$  is located at a higher volume than  $K$  in all odd-numbered plots, and at a lower volume than  $K$  in all even-numbered cases.

We now address the relation of the extremum  $R$  to the type of retrograde condensation. Take, for example, case 6. Coming down along a vertical path of fixed composition passing between points  $P$  and  $R$ , a mixture, on expanding, develops a drop of liquid when it enters the plait on the dew side of the

SIDE OF THE LARGE VOLUMES.

Temperature slightly *higher* than the critical temperature of the solvent.



SIDE OF THE LARGE VOLUMES.

Temperature slightly *lower* than the critical temperature of the solvent.

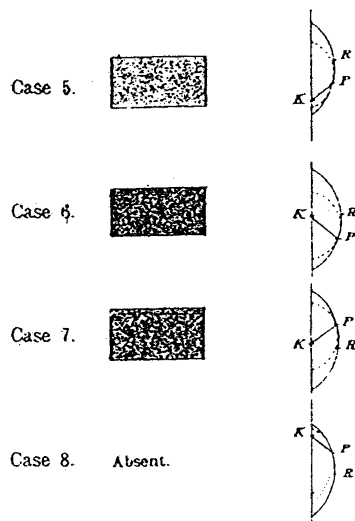


Fig. 11.4 Eight possible ways in which a plait forms by addition of a small amount of a second component to a fluid near its critical point. The vertical axis is the volume axis, the horizontal one the concentration.  $K$  is the critical volume of the first component,  $P$  is the mixture plait point, the full curve is the connodal,  $R$  is the extremum on the connodal, and the dashed curve is the spinodal. Copied from Korteweg (1903), Fig. 1.

connodal. On continued expansion, the amount of liquid grows, reaches a maximum, and then shrinks, to disappear when the mixture passes out of the plait, again on the dew side of the connodal. This is retrograde condensation of the first kind, as discovered and explained by Kuenen, see Ch. 6.6. Cases 3-6 are in this category.

In a case such as 7, on the other hand, the low-volume mixture of fixed composition will now enter and exit the two-phase region through the bubble curve. Thus it will form a gas bubble, which will disappear again on further expansion. This is retrograde condensation of the second kind, which Kuenen tried in vain to find experimentally (Ch. 6.7). Cases 1-2 and 7-8 fall in this category.

Korteweg derived these cases from the Van der Waals binary-mixture equation by expanding the isothermal Helmholtz energy at the critical point of the solvent in terms of concentration and volume. Korteweg needs to con-

sider only two parameters,  $a_{12}$  and  $b_{12}$ , since the application is to a dilute mixture to lowest order in concentration, when solute-solute interactions can be neglected, Korteweg introduces the lowest-order parameters

$$\kappa = a_{12}/a; \quad \gamma = b_{12}/b \quad (11.5)$$

and proceeds to calculate in which ranges of  $\kappa$ ,  $\gamma$  space the individual cases shown in Fig. 11.4 prevail. Note that this is the quite general 'global' problem, be it near the limit of infinite dilution. The geometric-mean rule is not assumed, nor is any restriction placed on the strength of the unlike excluded volume  $b_{12}$ .

A large color graph of these ranges and their borders in  $\kappa$ ,  $\gamma$  space accompanies the paper. A reduced-size copy, be it in black and white, is shown in Fig. 11.5. Even though the color of the original is lost, Fig. 11.5 is still easy to read, since the labels of the regions correspond to those in Fig. 11.4. Regions of negative  $\kappa$  or  $\gamma$  have no physical meaning.

Korteweg's (1903) paper gives the details of the calculations of the border curves in Fig. 11.4 to second order in concentration, based on a Taylor expansion at the plait point of the solvent, and finding the plait point of the mixture as discussed before, Ch. 5.3.6. Korteweg gives expressions for the initial shift of the plait point concentration as a function of temperature, and the shift of the plait point volume as a function of concentration. We will not discuss these derivations here. One result is that case 8 does not follow from the Van der Waals equation, which is the reason one does not find it in Fig. 11.5. A second result is that points on the border between regions with plaits open to the left and plaits open to the right, such as case 2 and case 6, correspond with a double homogeneous plait points (Ch. 5.4.2) at the solvent critical point. In Fig. 11.5, there is one point where six regions meet. This is the point where the mixture interaction parameters equal those of the solvent,  $\kappa = 1$ ,  $\gamma = 1$ , a pathological case, physically speaking, requiring a higher-order treatment.

Korteweg's work on the general dilute Van der Waals mixture is exact and exhaustive. It is to be regretted that it evolved independently from Verschaffelt's and Keesom's work. Korteweg refers often to their work and even refrains from claiming priority:

We do not, however, give them [the mathematical relations Korteweg presents] as new, as they must essentially agree with similar equations obtained by Keesom (1901) and Verschaffelt (1903).

An early collaboration with the Leiden scientists, especially Verschaffelt, might have made all parties involved more effective. Kamerlingh Onnes seems to have viewed Korteweg as a competitor, see Ch. 11.4.6.

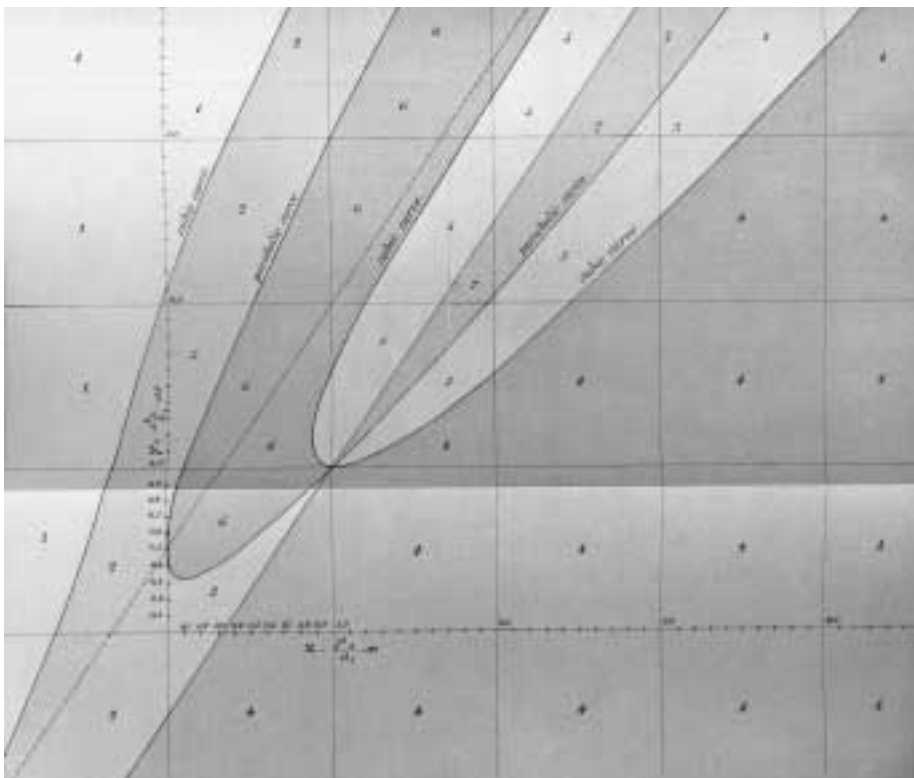


Fig. II.5 'Global' diagram for mixture behavior near the solvent critical point according to the Van der Waals equation. The regions in  $x$ ,  $\gamma$  space, with  $x = a_{12}/a$  and  $\gamma = b_{12}/b$ , in which the various scenarios shown in Fig. II.4 prevail according to the Van der Waals equations for mixtures. The numbers in Fig. II.4 correspond to those in Fig. II.5. Case 8 in Fig. II.4 does not occur in Fig. II.5. In the point  $x = 1, \gamma = 1$  six regions meet. Regions of negative  $x$  and  $\gamma$  have no physical meaning. Copied from Fig. 1, in color, of Korteweg (1903). The horizontal line just below the center is an artifact due to a fold in the original.

II.4.4 *Verschaaffelt: an experiment on dilute near-critical mixtures, and its interpretation.* We introduced Verschaffelt in Ch. 9, after he began to work on his doctorate at the Physical Laboratory in Leiden. Kamerlingh Onnes wanted him to study the system carbon dioxide-hydrogen. The initial objective seems to have been a more detailed study of retrograde condensation than Kuenen had done (Ch. 6.6). Another goal was to test the validity of the principle of corresponding states for mixtures. Serendipitously, the system became a model for impurity effects in which Kamerlingh Onnes was interested,

embroiled as he was in conflicts about the nature of criticality (Ch. 10). There were some experimental constraints. The critical pressure of carbon dioxide is over seventy atmospheres to begin with, and Verschaffelt noticed right away that adding 5 mol% hydrogen led to a huge increase in vapor pressure as the mixture condensed. The study of this system in glass cells near the carbon dioxide critical point was therefore by necessity going to be limited to small fractions of hydrogen.

A large difference in volatility will enhance impurity effects. So the system carbon dioxide – hydrogen was an excellent choice: the first component has a critical temperature of 404 K, while that of hydrogen is only 33 K.

Measurements were performed as described in Ch. 6.4. The highest pressures Verschaffelt (1899a) reports for a 5 mol% mixture are close to 120 atmospheres. *P-V* isotherms were measured at seven temperatures from 15 to 31°C. One striking result is the huge increase in pressure required to make the mixture condense. At 15°C, for instance, pure carbon dioxide condenses at about 50 atmospheres. The 5% mixture, however, begins to condense at 57 atmospheres, but fully converts into liquid only at 103 atmospheres. This clearly demonstrates the fierce resistance to mixing of these two components. The plait point temperature decreases about 4°C for a 5% admixture of hydrogen. Verschaffelt found clear evidence of retrograde condensation of the first kind.

Next, Verschaffelt (1899b) reports some results for the nominal 10 mol% and 20 mol% mixtures. For these, he could only measure short stretches of the *P-V* isotherms, because the pressure limit of his apparatus was quickly reached. From the data, he constructed the dew-bubble curves and the plait point curve. The latter keeps on moving to lower temperatures and to steeply higher pressures.

It is clear to us that Verschaffelt has inadvertently discovered a Type-III phase diagram (Ch. 7 and Ch. 8), with a critical line running to high pressure and lower temperatures. At that time, Kuenen had not yet published his work on such a system. Verschaffelt does wonder about the course of the plait point line. He thinks it will rise equally steeply from the hydrogen side and speculates that it may go through a very high maximum, suggesting an uninterrupted mixture critical line (Type I). Much later, however, in the French translation of his thesis, in 1906, he quotes Kamerlingh Onnes as suggesting that two branches of the critical line might rise steeply from the carbon-dioxide and hydrogen critical points and move to infinite pressure. This was just about the time Van Laar investigated the longitudinal plait, making connection with Kuenen's Type-III phase diagram (Ch. 7.5), although just before gas-gas equilibrium was discovered and explained in Leiden (Ch. 8). Verschaffelt (1906a), however, in a model described in Ch. 11.4.6, still calculates the critical line for the mixture of carbon dioxide and hydrogen as a continuous curve with a very

large pressure maximum. For the present application, the inappropriate phase diagram presents no problem, because only the part of the critical line close to the carbon-dioxide critical point is under consideration.

Verschaffelt (1900b) performs a test of the law of corresponding states by plotting the  $P$ - $V$  isotherms for pure carbon dioxide by Amagat, and for the 5%, 10%, and 15% mixtures he himself has obtained, on large-scale logarithmic plots, shifting these with respect to each other to make them superimpose, which he is able to do quite well. This procedure is an example of the use of empirical scale factors discussed in Ch. 3.5.

It is important to realize that the test is limited to a narrow range of temperatures, about 15°C, and that only the 5% mixture has substantial overlap with the isotherms of pure carbon dioxide. After superposition, even the closest 5% mixture isotherm is 7°C from the critical temperature of pure carbon dioxide; all other isotherms are further away after superposition. Verschaffelt notes some departures at densities higher than critical.

Verschaffelt obtains values for the critical parameters  $P_{xk}$ ,  $V_{xk}$ , and  $T_{xk}$  of each of the mixtures, the point at which the mixture would have become critical if a pure fluid, had it not become materially unstable. He calls these fictitious parameters the *critical parameters of the homogeneous mixture*. They will play a substantial role in Keesom's subsequent work.

Verschaffelt finds the concentration dependence of the scale factors. He also derives from the fictitious critical parameters the mixture parameters  $a_x$  and  $b_x$  that the Van der Waals equation would give, and finds that they can be represented as quadratic functions of the composition according to the mixing rules proposed by Van der Waals, Eq. (4.4).

11.4.5 *Keesom: dilute mixtures and the law of corresponding states.* Keesom (1901) wants to find out how the plait point shifts as an impurity is added to a pure host.

He first derives useful relationships between these slopes and derivatives of the pressure that could, in principle, be obtained from experiment. In the back of his mind is Verschaffelt's experiment, in which  $P$ - $V$  isotherms were obtained for mixtures of constant concentration. Although such experiments readily yield the 'fictitious plait point,' they give no clue as to the location and shift of the real plait point.

Keesom first performs a service to science by writing Van der Waals's (1895) expression for the initial slope of the plait point temperature in a more convenient way. He replaces Van der Waals's second derivatives of the energy and free energy by derivatives of the pressure. Keesom then produces the following relation for the initial change of the (real) plait point temperature with composition:



W.H. Keesom and J.P. Kuenen posing at the rear of the Physics Laboratory, Leiden in 1909. Keesom is the tall bearded man next to the door. Kuenen is the one flanking the woman (Miss G.L. Lorentz). Collectie Academisch Historisch Museum, Universiteit Leiden. Copied with permission.

Lim ( $x \rightarrow 0$ , solvent critical point)

$$dT_{pl}/dx = -\frac{(\partial P/\partial x)_{VT}^2 + RT (\partial^2 P/\partial x \partial V)_T}{RT (\partial^2 P/\partial T \partial V)_T} \quad (11.6)$$

Keesom's equation thus permits evaluation of the initial slope of the plait point temperature from first and second derivatives of the pressure, evaluated at the solvent critical point. Alternatively, once an equation of state is given for the dilute mixture, the derivatives at the solvent critical point can be evaluated. Although the sign of the denominator is always negative, the plait point temperature may rise or fall depending on the sign of the second term in the numerator and the magnitude of this second term compared to the first. Keesom's nice result was forgotten and derived anew by American chemical engineers Redlich and Kister (1962).

Keesom (1901) presents an expression similar to Eq. (11.6) for the initial change of the plait point pressure (his Eq. 1C, p. 295) with concentration. The two derivatives are related by the expression:

$$\begin{aligned} &\text{Lim } (x \rightarrow 0, \text{ solvent critical point}) \\ &dP_{\text{pl}}/dx = (\partial P/\partial x)_{VT} - (\partial P/\partial T)_{Vx} dT_{\text{pl}}/dx \end{aligned} \quad (11.7)$$

with  $dT_{\text{pl}}/dx$  standing for the right-hand side of Eq. (11.6). Keesom's more elaborate expression represents Eq. (11.7) with  $dT_{\text{pl}}/dx$  substituted from Eq. (11.6).

In the limit  $x \rightarrow 0$ , the derivative  $(\partial P/\partial T)_{Vx}$  equals  $(\partial P/\partial T)_V$ , the limiting slope of the critical isochore, which is the locus  $V = V_c$  of the pure solvent. Keesom now makes use of the fact that in the  $P$ - $T$  plane at the critical point, the critical isochore and the vapor pressure curve of a one-component fluid are confluent, see Fig. 11.2. He mentions that Van der Waals proved this interesting equality in his lecture notes, and that Van Laar and others also noted it. In part 3 of his paper, Keesom (1901) copies three proofs given to him by Van der Waals. Later, Van der Waals (1905b) will finally publish these proofs, see Ch. 11.4.8. Keesom uses the equality of  $(\partial P/\partial T)_V$  and  $(dP/dT)_\sigma$  at the critical point for numerical estimations of one or the other of the two. Usually the latter is easier to obtain from experiment. If  $(dP/dT)_\sigma$  is substituted for  $(\partial P/\partial T)_V$ , Eq. (11.7) could have been written as

$$\begin{aligned} &\text{Lim } (x \rightarrow 0, \text{ solvent critical point}) \\ &dP_{\text{pl}}/dx = (\partial P/\partial x)_{VT} - (dP/dT)_\sigma dT_{\text{pl}}/dx \end{aligned} \quad (11.8)$$

Keesom retains the right-hand side of Eq. (11.6) for  $dT_{\text{pl}}/dx$  in his expression.

Krichevskii (1967) derived Eq. (11.8) anew. Krichevskii, who rekindled the interest in dilute near-critical mixtures in the modern age, led a large experimental group in the area of fluid mixtures in the former Soviet Union. This group is known for several firsts, such as the measurement of gas-gas equilibrium above the component critical points (Ch. 8), and of the tricritical point (Ch. 7.2.4). The infinite-dilution critical value of  $(\partial P/\partial x)_{VT}$ , a non-diverging characteristic indicator of dilute-mixture behavior near the solvent critical point, is presently called the *Krichevskii parameter*.

Keesom (1901) now proceeds to estimate the various derivatives in Eq. (11.6) in order to test his relationship. He estimates numerical values for the slopes of the vapor pressure curve and the critical isochore from experiment. For carbon dioxide, he reports a value near 7, in reduced units, with a 10% spread. The spread makes him unhappy. Discreetly, Keesom does not mention that the Van der Waals equation gives a value of only 4 for  $(dP/dT)_\sigma$ .

After 1900, everyone involved, including the master himself, seems to be content with the experimentally derived value of 7 for this slope.

For the derivative in the denominator of Eq. (II.6),  $(\partial^2 P/\partial T \partial V)_T$ , Keesom derives a value from Amagat's data on carbon dioxide, which happens to agree closely with that from the Van der Waals equation. (If, however, the value of  $(\partial P/\partial T)_V$  is uncertain by 10%, there is no way he could have derived the volume derivative of this quantity with an uncertainty even approaching 10%.)

More seriously, but unknown to Keesom, or anyone else at that time, this particular second derivative must be *zero* in a real fluid at its critical point because of the failure of mean-field theory at the critical point, (Ch. 9). Thus, Eq. (II.6) is not applicable to real fluids. If care is used in taking the infinite-dilution limit, however, Eqs. (II.7) and (II.8) do retain their validity for real fluids.

Having been unsuccessful in a direct test of Eq. (II.6) due to circumstances beyond his control, Keesom decides to rewrite this equation in terms of the law of corresponding states. He uses the fictitious gas-liquid critical parameters mentioned in connection with Verschaffelt's work to make the pressure, volume, and temperature dimensionless

$$\pi = P/P_{xk} \quad \tau = T/T_{xk} \quad \omega = V/V_{xk} \quad (\text{II.9})$$

In these reduced coordinates, the mixture obeys the same equation of state as the pure fluid. Keesom expresses all derivatives on the right-hand side of Eq. (II.6) in terms of these reduced coordinates, in the limit of small  $x$  near the solvent critical point, and obtains the following result:

$$(1/T_k) (dT_{pl}/dx) = \alpha - \frac{[\beta - \alpha (\partial\pi/\partial\tau)^2]}{C (\partial^2\pi/\partial\omega\partial\tau)} \quad (\text{II.10})$$

with a corresponding expression for the initial slope of the pressure along the plait point curve. The constant  $C$  represents the value of the inverse critical ratio. The derivative  $dT_{pl}/dx$  and  $dP_{pl}/dx$  are thus expressed in terms of derivatives of the reduced, one-component equation of state, with two parameters characteristic of the mixture:

$$(1/T_k) (dT_{xk}/dx) = \alpha; \quad (1/P_k) (dT_{xk}/dx) = \beta \quad (\text{II.11})$$

At first sight, it seems a step backward to express the concentration dependence of the *real* plait point temperature in terms of that of the *fictitious* plait point. The advantage of Eq. (II.10) is, however, that the derivatives involved are those of a pure component. Contrary to Eq. (II.6), no concentration derivatives are involved. Moreover, Verschaffelt (1900) had already

shown the way to obtaining the fictitious plait point parameters, namely by superimposing the measured  $P$ - $V$  isotherms of the mixture of constant composition onto those of the pure solvent using two scale factors. Keesom also derives a simple relation for the location of the real plait point in  $P$ - $T$  space with respect to the fictitious plait point for small  $x$ :

$$\frac{P_{pl} - P_{xk}}{T_{pl} - T_{xk}} = (dP/dT)_\sigma \quad (11.12)$$

This is a result that Van 't Hoff should have appreciated: since the right-hand side is a pure-solvent property, the ratio on the left must be the same for all solutes in the same solvent. Keesom estimates the left-hand side of Eq. (11.12) using Verschaffelt's values (1899c, 1900b) for 10% and 5% hydrogen in carbon dioxide. He is content with a 20% mutual agreement of the left-hand and the right-hand side of Eq. (11.12).

Although he had already demonstrated the futility of pinning down second pressure derivatives, he wrestles through the computations required to calculate the shift of the plait point *volume* with composition in the last pages of this paper. This leads to a formula occupying a full three lines on a page. It contains various third derivatives of the reduced pressure, and can obviously not be tested.

The paper ends with the honest admission that there are not enough sufficiently accurate data to test the expressions derived for the shift of the plait point parameters. For the comparison of observation and calculation, Keesom considers the simple Eq. (11.12) the most important result for the time being. That so much effort has yielded such minimal returns must have been a painful conclusion for the Leiden proponents of the law of corresponding states.

11.4.6 *Verschaffelt models dilute near-critical mixtures.* Shortly after Keesom's (1901) work was published, Verschaffelt (1902a, 1902b, 1903) took up the same problem. Inspired by Keesom's work, Verschaffelt (1902a) decides to use the law of corresponding states in the form of the two-scale-factor empirical virial equation developed by Kamerlingh Onnes (Ch. 3.5) that was fitted accurately to data for several pure fluids.

Verschaffelt then develops a Taylor expansion of the virial equation for the pure solvent at the critical point, and proves that the coexistence curve is a parabola to lowest order. Verschaffelt does not show any reluctance to do this, even though he was the only person to know that such an expansion is not possible (Ch. 9.4.4), and he does not allude to his finding that this curve is a cubic.

Next, Verschaffelt expands the mixture equation of state, at constant composition, around the fictitious critical point. He expresses the expansion coefficients in terms of the shift of the critical parameters, which he knows empirically from his superposition of isotherms. Alternatively, he can obtain them from Kamerlingh Onnes's reduced virial equation.

Although Korteweg (1903) would calculate the coefficients of the expansion from the Van der Waals equation, Ch. 11.4.2, while Verschaffelt uses the empirical virial equation, once the expansion is performed, further mathematical procedures are the same. Nevertheless, the Amsterdam mathematician and the Leiden physicist worked independently during the same time period. Verschaffelt's work can be considered to be the more general because it is not based on the Van der Waals equation.

Verschaffelt's (1902a, 1902b) papers, published as Leiden Comm. 81, consist of a thick sheaf of calculations of the behavior of a dilute mixture near the solvent's critical point. Verschaffelt could have learned from the clarity of presentation that marks Korteweg's work.

A letter from an unhappy Kamerlingh Onnes (1903) to Verschaffelt, dated January 24, reveals that there is a problem with the draft of Leiden Communication 81, which was to bundle Verschaffelt's (1902a, 1902b) papers. Korteweg had presented his results in the December 1902 meeting of the Academy, and apparently reported that there were some discrepancies with Verschaffelt's results. Korteweg (1903), however, while referring repeatedly to the work of Verschaffelt and Keesom in the publication, did not mention any discrepancies. We quote from Kamerlingh Onnes's (1903a) letter to Verschaffelt:

You have everywhere expanded to a power one higher [than Korteweg]. You remember that I explicitly cautioned you about this approach, because lots of powers might then be needed, and you understand that I do not have the time to do such a thing, or check it. But I do advise you to check once more all calculations....

...Could you not work through all of Korteweg's essay with your new results, expressing all of Korteweg's coefficients in yours and then comparing all of Korteweg's conclusions with yours? This would be very useful by itself. But it would be very useful indeed if you would in time discover a mistake in your calculations, as far as they don't agree with Keesom's and the latter have been checked. Surely it is also desirable for you to draw your cases in the  $xV$  plane and it is regrettable that you have not worked right away on the representation in the  $\psi$  [Helmholtz energy] plane, but have let yourself be distracted by other problems, because since Korteweg has entered this field, you should understand that it would have been desirable that you would have made of it what you could.....I am holding back Comm. 81 for the time being. [Translated from the Dutch.]

(The ‘other problems’ must refer to Verschaffelt’s discovery, discussed in Ch. 9.4.4, of the failure of mean-field theory at the critical point.) In a letter of Kamerlingh Onnes (1903b) to Verschaffelt dated February 18, it appears that Verschaffelt had great difficulty trying to fit the adjustable parameters of the virial-equation corresponding-states model. When fitted to all data, the resulting critical point was in the wrong place. Kamerlingh Onnes agrees that there is something discrepant between the behavior of the fluid in general and near a critical point (something Verschaffelt had tried to convey to him repeatedly, Ch. 9).

There is definitely something irreconcilable between the critical region and the isotherms further away. The conflict between what follows from the isotherms further away and the observations nearby the critical temperature indicates that in the critical region the observations are dominated by influences not yet clarified. [Translated from the Dutch.]

He feels, however, that reasonably close to a critical point the virial model should still be able to represent qualitatively the difference between pure-fluid and mixture behavior, since if there is deviant behavior, it would be the same for all substances. Dutifully, Verschaffelt (1903) carries out the substantial chore of an intercomparison with Korteweg’s results, substituting Korteweg’s Van der Waals equation for mixtures by his own empirical virial equation. After correcting a few mistakes in his 1902 papers, he finds complete agreement with Korteweg’s results. Later, however, Verschaffelt (1906b) published yet another erratum: he had found that some small terms were omitted in the starting expansion of the mixture free energy.

Verschaffelt must be pitied. Keesom had worked on this problem, and had already decided that the data were not good enough to obtain the necessary values of pressure derivatives. Verschaffelt had to work with a model that he alone knew was wrong at the critical point. Fitting the data in a reasonable way appeared impossible. A monstrous amount of formula manipulation had to be carried out. He found himself in a race with Korteweg and under pressure by Kamerlingh Onnes.

As stated in Ch. 10.16.2, Verschaffelt (1904) totally redeemed himself in Kamerlingh Onnes’s estimation by making the first useful estimate of the size of impurity effects in Teichner’s (1904) questionable experiment. He used a net of isotherms for mixtures of carbon dioxide and oxygen determined by Keesom in the work for his doctoral thesis; Keesom had superimposed these isotherms following Verschaffelt’s example (Ch. 11.4.5), and had estimated the parameters  $\alpha$  and  $\beta$  in Eq. 11.11. A pure fluid and a dilute mixture at the same pressure and temperature are at slightly different values of the reduced coordinates. To lowest order, the reduced temperatures differ by  $\alpha x$ , and the reduced

pressures by  $\beta x$ . The corresponding density differences can then be directly obtained from the reduced plot of the  $P$ - $V$  isotherms. Verschaffelt estimates that, in the absence of stirring, Teichner must expect a density gradient of the order of 30% over the length of the tube if there is a concentration difference of 0.001 mole fraction between the ends. Thus, Verschaffelt obtained by simple means a useful estimate of the magnitude of impurity effects in near-critical fluids. Kamerlingh Onnes's praise for this work was quoted in Ch. 10.16.2.

11.4.7 *Van Laar uses the geometric-mean Van der Waals model.* Van Laar (1905h) felt compelled to react to a paper by Van 't Hoff (1903) about the rise of the critical (plait point) temperature due to the addition of a solute in the limit of infinite dilution. True to form, Van 't Hoff had stated that this rise was universal, the same for a mole of any solute. Van Laar (1905h), however, derived an approximate expression for the rise of the critical-point temperature, which clearly depended on the Van der Waals parameters of the solute in question and thus lacked Van 't Hoff-like dilute-mixture universality. Dissatisfied about a very unreasonable assumption he had to make in order to fit his expression to known data, Van Laar (1905e) begins anew. He knows about Keesom's exact expression, Eq. (11.10), based on the law of corresponding states, but criticizes it as containing too many derivatives that have to be obtained empirically. He, in his turn, uses his own exact expression (Ch. 7.5.4) for the plait point curve for Van der Waals mixtures obeying the geometric-mean rule, Eq. (4.7), for mixtures of arbitrary  $a$  and  $b$ . After elaborate calculations, he obtains a compact expression for the change of the critical temperature with composition at infinite dilution:

$$(1/T_1) (dT_{pl}/dx)_{x=0} = \theta \pi^{-1/2} \{ \theta \pi^{-1/2} (3/2 - \pi^{-1/2}/2)^2 - 1 \} \quad (11.13)$$

with  $\theta = T_{c2}/T_{c1}$ , the ratio of the critical temperature of the solute to that of the solvent, and  $\pi = P_{c2}/P_{c1}$ , the ratio of the critical pressures. This expression is not only simple, it is also highly useful, since the rise of the critical temperature is now expressed for the first time in terms of directly measurable pure-fluid critical properties only, be it under the restriction of the geometric-mean rule. The expression simplifies even more if it is assumed that the critical pressures of the host and the impurity are the same. Then, the right-hand side reduces to  $\theta(\theta-1)$ .

Van Laar (1905e) makes an interesting comparison of Eq. (11.13) with experiment. It so happened that Bakhuis Roozeboom's graduate student Büchner had performed one of the first experiments on supercritical solubility. Five organics of low volatility, such as naphthalene and tribromomethane, were dissolved in carbon dioxide near its critical point. The solubility is, by definition, the concentration at which the solution saturates in

the presence of an excess of the solute. At saturation, the plait point curve reaches a critical end point that is usually close to the critical point of the solvent. From the solubility and the temperature at the critical end point, Van Laar readily obtains an estimate of the value of  $(1/T_1) dT_{pl}/dx$ . In order to calculate  $\theta$ , the critical temperature of the solute is needed, which was not known for any of these solutes. Van Laar poses as a rule of thumb that the critical temperature equals twice the melting temperature. Van Laar finds agreement between the experimental value of  $(1/T_1) dT_{pl}/dx$ , and his  $\theta(\theta-1)$  rule on the level of 20% or better. Why was he so lucky? For one, he refrained entirely from calculating any property involving the volume, which would have come out poorly. For another, there was no need for him to take derivatives of experimental data. This was a nice piece of work, with an interesting new application.

II.4.8 *Van der Waals has the last word.* Van der Waals (1905a,b,c) begins a series of three papers in the following irritated vein:

..., by a remark by Van 't Hoff, and by Van Laar's calculations, a discussion has been carried on on the rise of the critical temperature of a substance in consequence of an admixture. In this it has been perfectly overlooked that already more than ten years ago, the principal properties of the critical line, and also the properties at the beginning and the end of the line were discussed and determined by me.

In this first paper, Van der Waals begins with his 1895 expression referred to in Ch. II.4.1, which gives the initial rise of the critical temperature in terms of second and third derivatives of the Helmholtz free energy. Using his mixture equation of state, he is able to obtain an expression in terms of infinite-dilution concentration derivatives of the characteristic parameters  $a$  and  $b$ , valid for the case that  $b$  is a constant. He spends some effort reworking it, approximating some of the terms, and trying to compare with Keesom's experimental data on the mixture of carbon dioxide and oxygen. That leads him to an expression akin to that Krichevskii would derive much later, Eq. (II.8), except that instead of the initial slope of the plait point curve, his expression is derived for the initial slope of the line of *fictitious* critical points. This leads him into the same blind alley as Keesom and Verschaffelt.

The paper suffers from repeated switching between calculations based on the Van der Waals pure-fluid and mixture equation of state, and comparisons based on empirical fact. The fact that the excluded volume must shrink as the density increases, for instance, is not incorporated in the equation of state, leading to a 30% overestimate of the critical volume. Furthermore, Van der Waals uses the empirical fact that the slope of the pure-fluid vapor pressure curve is around 7, while his equation of state gives a value of only 4.

In the second paper, Van der Waals (1905b) follows a much more satisfactory path. Apparently, he paid attention to Keesom's remark that all kinds of useful but unpublished thermodynamic relations at the solvent critical point could be found in Van der Waals's lecture notes (see Ch. 11.4.5), and he sets out to neatly derive these relations one by one. Thus, there is a proof of the pure-fluid property that the critical isochore and the vapor pressure curve in the  $P$ - $T$  plane have the same slope at the critical point.

In the same paper, a number of interesting dilute-mixture properties are described that would be slowly rediscovered in the 1960s and 1970s (see Ch. 11.4.5). First, there is the proof that the dew and bubble curves in the  $P$ - $T$  plane have a common tangent at the pure-solvent critical point, the 'bird-beak' effect, see Fig. 11.3, (b). It is also shown that this slope is equal to the derivative  $(\partial P/\partial x)_{V,T}$  at the solvent critical point.

Another interesting relation is that between this derivative, the solute concentrations  $x_1$ ,  $x_2$  in coexisting phases, and the molar volumes  $V_1$ ,  $V_2$  of the two phases near the solvent critical point:

$$(\partial P/\partial x)_{V,T} = RT [(x_2 - x_1)/x_1] [1/(V_2 - V_1)] \quad (11.14)$$

Since the left-hand side of Eq. (11.14) remains finite as  $x_1$  and  $x_2$  tend to zero,  $x_2 - x_1$  must approach the value of zero faster than  $V_2 - V_1$  does. This was noted in Ch. 11.3.3, and shown in Fig. 11.1, (b).

The last of the three papers is an excruciating attempt to fit expressions for limiting behavior to measured mixture properties. Van der Waals (1905c) makes no secret of the fact that, although he needs an equation of state to evaluate several of the derivatives in his expressions, large deviations must be expected especially in volume-related properties, due to the neglected volume dependence of the excluded volume  $b$ . The large departure of the experimental slope of the vapor pressure curve from that predicted by his equation is also referred to. A number of attempts to obtain numerical estimates for infinite-dilution properties follow, with Van der Waals alternating between the equation of state and empirical parameters, interspersed with data comparisons. There do not seem to be new results in this paper and it ends without a firm conclusion.

11.4.9 *An evaluation.* Van 't Hoff's work honed scientists' interest in dilute solutions. Almost all members of the Dutch School participated in the studies of dilute mixture effects near critical points described in this chapter. The results fall into three classes: thermodynamic relationships between various properties of dilute mixtures near the plait point; calculations by means of the Van der Waals equation for mixtures; and calculations by means of the law of corresponding states.

As to the thermodynamic relationships, Van der Waals was clearly the leader, setting the tone with his early formulae for the change of temperature and pressure along the plait point curve, and later, proving interesting relations for properties of coexisting phases in a mixture near the host's critical point. Keesom contributed heavily by rewriting Van der Waals's formulae in terms of experimentally accessible variables.

The calculations based on variants of the Van der Waals equation for mixtures are relatively simple, because the interactions between solute molecules are negligible to lowest order. Korteweg's application is general, elegant and complete. The mathematician was not as close to experiment as Van Laar and his Leiden colleagues, which limited the impact of his work. Van Laar's geometric-mean Van der Waals model is both simple and applicable.

Keesom's and Verschaffelt's contributions on the basis of variants of the law of corresponding states were sound in principle, but application was a disappointment. This was due in part to the impossibility of estimating reliable values for second derivatives of experimental data. More seriously, however, the inadequacy of a mean-field description of near-critical states in pure fluids and in mixtures played a role. Verschaffelt and Kamerlingh Onnes sensed this, but more than half a century would pass before this issue was resolved. From a modern perspective,  $P$ - $V$  isotherms of fluid mixtures of constant concentration cannot be expected to superimpose near a critical point: a field variable, not a density, must be kept constant for critical-point universality to hold.

For a rough estimation of impurity effects, Verschaffelt's and Van Laar's shortcuts paid off. Verschaffelt's repeat of Korteweg's calculations for a corresponding-states model, this time to third order, however, was not a good idea. Given the limited computational means of the times, mistakes were unavoidable. More seriously, Keesom had already shown the inadequacy of that approach even at the second-order level.

The present-day reader is appalled by the extraordinary calculative efforts made at that time. Modern computers do the work carried out with so much dedication a century ago, and our appreciation for such 'drudgery' is very limited. We should not forget that the Dutch school generally kept proper perspective, and that new concepts and deep insights emerged from the many pages of calculations. Appreciation of the historical work returns when one watches the old concepts and insights slowly rediscovered in modern times.

## 11.5 *Supercritical fluids*

In the 1980s there was a strong surge of interest in the behavior of mixtures near the pure-solvent critical point. The interest was driven by the unusual solvent properties of supercritical fluids, which could be made good use of in chemical process design. A decade earlier, however, Krichevskii and his experimental group in the Soviet Union did significant work, as did the American theoretical chemist John C. Wheeler.

From reviews by Krichevskii (1967) and Khazanova and Sominskaya (1971), it is clear that Krichevskii's group had spent considerable effort in order to obtain an experimental and a theoretical understanding of the behavior of dilute near-critical mixtures. A collaborator, Rozen (1976), worked out the thermodynamics of such systems by means of a classical Taylor expansion around the solvent critical point, in the way Korteweg or Van Laar could have done it. In the introduction to this paper, Rozen describes how Krichevskii was questioning whether the dilute-mixture laws would hold at the solvent critical point as early as 1943. Rozen then showed that the partial molar volume of the solute, instead of varying linearly in the concentration, diverges as  $x^{-1/3}$ . This follows immediately from Eqs. (11.3) and (11.4). Initially, Krichevskii refused to believe this, but measurements from his own group confirmed the divergence. Even stranger, these measurements also demonstrated that the partial molar volume of the solvent does not simply become equal to the molar volume of the solvent, but has different limits at the solvent critical point depending on the path of approach. Rozen (1976) worked out these different limits under the mean-field assumption.

Wheeler (1972) had reached this same conclusion on the basis of a non-classical theoretical model. An expert on decorated lattice gases, he calculated the partial molar volume near criticality for a modern nonclassical version of the decorated lattice gas. The partial molar volume of the solute indeed diverges, be it with a different exponent than in Rozen's case for the mean-field fluid. Wheeler (1972) also rediscovered the 'bird-beak' behavior of the dew-bubble curve, Fig. 11.3, (b). In addition, Wheeler confirmed that the limiting value of the *solvent* partial molar volume depends on the path to the solvent critical point, and he gave the proof for his model.

The partial molar properties of the solute are the mainstay of solution chemical thermodynamics. They are directly connected to the infinite-dilution standard state first characterized by Van 't Hoff, and are extensively tabulated for many aqueous systems. This unanticipated divergence of the standard state was an unpleasant surprise. It implies that at the solvent critical point, the departures of the solution from the infinite-dilution state do not depend linearly on the concentration of the solute, but are unexpectedly large.

Many experiments performed in the 1980s have confirmed these divergences of the solute's partial molar properties at the solvent critical point. Highly accurate measurements of partial molar enthalpy and heat capacity of aqueous salt solutions, performed close to the water critical point at 647 K, revealed steep changes at low concentration, and the more so the closer to the water critical point. For reviews and references, see Levelt Sengers (1991, 1993).

A satisfactory formulation of the properties of solutions near the solvent critical point will be difficult to come by. Models such as those of Korteweg and Rozen are consistent and incorporate the anomalous behavior correctly at the mean-field level. However, if an accurate representation of the real, nonclassical fluid behavior is desired, an approach based on mean-field equations, or on the use of the traditional law of corresponding states must fail. For non-electrolytes, nonclassical mixture models are presently available, but most of these are limited to regions close to the critical point. The appropriate renormalization-group calculations incorporating charge screening effects in electrolyte solutions have not been performed as yet.

The Dutch scientists studied a problem with implications and challenges that they could not have foreseen. The difficulties they encountered when comparing with experiment resulted to a great extent from the nonclassical behavior of real fluids, only dimly perceived at that time. The Dutch School had reached the limits of mean-field theory, but did not have the means to transcend it.

