

Part I

PHASE EQUILIBRIUM

CHAPTER I

EARLY METHODS OF GAS LIQUEFACTION

I. 1. 1. *December 1877*

On 2 December 1877 Louis Cailletet, an engineer of Châtillon-sur-Seine, wrote the following letter to Sainte-Claire Deville: “Without losing a minute I hasten to inform you that I have to-day liquefied carbon-monoxide and oxygen. Maybe I am mistaken when I say ‘liquefied’, for at a temperature of -29° , obtained by evaporating sulphur-dioxide, and at a pressure of 200 atmospheres, I saw no actual liquid; but under these conditions so thick a mist appeared that I concluded it was vapour near the point of liquefaction....”

On 22 December the secretary of the French Academy of Science received a telegram from Geneva: “Oxygen liquefied to-day at 320 atm. and 100 degrees cold with sulphur dioxide combined with carbon dioxide Raoult Pictet.”

These events, which we now consider as marking the first step into a new domain of science, appeared at the time as the culmination of half a century’s concentrated labours. When in 1823 Faraday heated chlorine hydrate at one end of a closed V-shaped test-tube, producing liquid chlorine at the other end, little or nothing was known concerning liquid vapour equilibrium. After a number of gases had been liquefied at room temperature by simple compression, scientists were at a loss to account for the failure of this method when applied to oxygen and hydrogen. As the influence of temperature was dimly realised, various investigators began cooling their gases with the slender means then available, but no positive results

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were obtained. The expression “permanent gases” was coined, though Faraday himself was firmly convinced that all gases could be liquefied at sufficiently low temperatures.

The immense technical possibilities offered by the liquefaction of gases, which have in recent years induced industrial concerns to invest millions in liquefaction and rectification plants, had in the first half of the nineteenth century occurred to no one. To obtain air in the liquid state was a purely scientific problem and engrossed a number of the best scientists of the time, whose work was followed with intense interest by the whole scientific world.

Falteringly, as a result of innumerable unsuccessful experiments the laws of phase equilibrium were made plain. It was in the course of investigations on liquids with much higher boiling points than air that Cagniard de la Tour lighted on critical phenomena. The disappearance of a meniscus in the middle of a closed tube when the liquid was heated suggested a limiting temperature above which no increase of pressure can lead to liquefaction in the ordinary sense of the word, i.e. to the sudden formation of a new phase. The general lines of liquid vapour equilibrium were laid down in 1863 as the result of Andrews' work. Andrews' CO_2 isothermals have appeared in so many textbooks that it seems unnecessary to reproduce them here. They contain almost everything that is to be said on liquid vapour equilibrium of one-component systems. The results may be summarised briefly as follows:

- (1) Every one-component gas possesses a well-defined critical temperature, characterised on the corresponding p - v isothermal by a point of inflexion, the tangent to which is parallel to the v -axis.
- (2) The co-ordinates of the point of inflexion on the critical isothermal determine the critical pressure and critical volume of the gas.
- (3) At temperatures below the critical, the gas may be liquefied by simple compression, the pressure remaining constant during liquefaction. The coexistent phases thus appear as horizontal straight lines in the corresponding isothermals, when v is chosen as the axis of abscissae.

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The pressures needed to liquefy a gas are not high. The critical pressures of the so-called permanent gases are less than 50 atm. and those of most liquids apart from molten metals do not exceed 100 atm.

- (4) The further the temperature is lowered below the critical, the smaller the pressure needed for liquefaction.
- (5) Compression along the critical isothermal leads to complete liquefaction at the critical point without change of volume.
- (6) At temperatures above the critical, isothermal compression does not lead to the formation of a coexistent liquid phase. Though the density may be increased far above the critical, the substance remains homogeneous. By lowering the temperature of the compressed gas below the critical, it may be brought continuously to a state that is obviously liquid without passing through a region of two coexistent phases. There is therefore no point in differentiating between gas and liquid at temperatures and pressures above T_c and p_c .

To avoid an error that frequently occurs it should be remarked that the critical isothermal differs in no respect from other isothermals except at the critical point. No sudden change occurs in the properties of the substance in passing through the critical isothermal at any other point.

The knowledge of these facts revealed as the first problem in the liquefaction of the “permanent” gases the determination of their critical constants. Simultaneously a second problem had to be solved: by what means can the conditions necessary for liquefaction be produced? Experiments had already made it evident that the critical temperatures of these gases are low, lower in fact than those that could at the time be produced in the laboratory. Thus the liquefaction of gases became identical with the production of low temperatures.

The events that led up to and followed Cailletet’s famous letter are described very vividly by Georges Claude, himself an old pioneer, who can still recall the tense excitement roused by the discovery. While Cailletet was compressing acetylene in a glass tube with a powerful hydraulic press driving a

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column of mercury, a valve was accidentally left open. The pressure was thus suddenly relaxed; the expanding gas drove the mercury down the tube and was cooled so far as to show a thick mist of condensing liquid. Cailletet, who was repeating Andrews' experiments, was quick to perceive what had occurred. He repeated the experiment with oxygen, cooled previously with evaporating sulphur dioxide, and the result is contained in his letter to Sainte-Claire Deville. In his book, *Air Liquide, Oxygène, Azote*, Claude describes how Cailletet refrained from making his discovery public at the next meetings of the French Academy. He had been proposed as a corresponding member and did not wish to bias the voters by a sensational publication before the election. On 24 December the announcement of his discovery was to take place. Two days earlier the Academy received Pictet's telegram, stating that he had liquefied oxygen. The letter to Sainte-Claire Deville is the only proof of Cailletet's priority.

Cailletet's experiment can hardly be said to have solved the problem of air liquefaction. Under his conditions a few drops of liquid could at the best be produced, which must needs evaporate the moment the expansion ceased. However, in view of the fact that this method has of late in a modified form become of importance for the liquefaction of helium, it may be well to show how a simple calculation may roughly account for Cailletet's result. Suppose that we may as a first approximation neglect the transmission of heat from the gas to the mercury and to the glass walls of the tube, an assumption that might be justified if the expansion were sufficiently rapid, then our case is a simple adiabatic expansion, for which the First Law gives the differential equation

$$du = -p dv, \quad q \text{ being zero.}$$

Assuming the gas to obey Boyle's law under the conditions of the experiment, an hypothesis which is of course far from correct, and taking v and T as independent variables, we have

$$C_v dT = -RT/v dv.$$

Separating v and T , we may integrate the equation and obtain

$$\log T_1/T_2 = R/C_v \cdot \log v_2/v_1 = R/C_p \cdot \log p_1/p_2.$$

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The molal heat of oxygen at constant pressure is approximately $7R/2 \sim 7 \text{ cal./}^\circ$; p_1 in Cailletet's case was in fact 300 atm. and T_1 about 250° K . Inserting these figures, we obtain

$$\log 250/T_2 = 2/7 \log 300 \sim 0.7,$$

which gives $250/T_2 \sim 8.5$ or $T_2 \sim 29^\circ \text{ K}$.

We now know that the normal boiling point of oxygen is 90° K . It is thus plainly within the bounds of possibility to produce liquid oxygen by Cailletet's method. But as the latent heat of evaporation of oxygen is 1600 cal./gramme-molecule, it is not surprising that only a few drops are obtained.

We have already stated that Pictet very nearly forestalled Cailletet in liquefying oxygen. His work is important not only in exemplifying the laws of phase equilibrium but because the method he first employed, and which was later perfected by Kamerlingh Onnes in Leiden, has proved a most powerful instrument for air liquefaction in the laboratory.

In Pictet's so-called Cascade Process the low temperature needed for the liquefaction of oxygen is obtained gradually in the course of several stages. In the first a gas easily liquefied at room temperature is condensed under pressure and expanded into a separate low-pressure chamber, in which the vapour is pumped back to the compressor, the gas thus circulating through the system. Through evaporation the temperature in the low-pressure chamber can be reduced below the critical point of a second gas. In the second stage this second gas can then be condensed and thereupon cooled in a second low-pressure chamber by evaporation. The process may be continued until the critical temperature of oxygen is reached; and in this way air, nitrogen and carbon monoxide may be liquefied.

Pictet in his first experiments used SO_2 in his first circuit and CO_2 in the second. In the low-pressure chamber of the CO_2 circuit the liquid carbon dioxide was solidified and cooled by sublimation. Oxygen at high pressure was admitted to a tube immersed in the solid CO_2 and then released through a valve to the atmosphere. Pictet describes how a jet of liquid oxygen shot through the valve and immediately evaporated. However, though he himself believed that a temperature of -140° C . in the CO_2 was reached, it is almost certain that it remained

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above -110°C . As the critical temperature of oxygen is now known to be -118° , we must conclude that the liquid oxygen was formed on releasing the pressure as in Cailletet's experiment.

In Kamerlingh Onnes' cascade at Leiden, which was working until quite recently and with the help of which all the notable cryogenic experiments were carried out, the first circuit contained methyl chloride, the second ethylene and the third oxygen.

I. 1. 2. *The Cracow School*

The first experiments of Cailletet and Pictet were followed almost immediately by the installation at Cracow in Poland, then in the Austrian province Galicia, of a cryogenic laboratory in the most advanced sense of the word. Here Wroblewski and Olszewski, equipped with highly efficient scientific apparatus, proceeded to "create" Low Temperature Physics. From a glance at any of Olszewski's papers of the early eighties the purpose of these experiments is immediately evident. A few drops of fog in a tube and an evaporating jet of liquid are no basis for scientific research. What we need is a liquid "boiling quietly in a test-tube", which we can observe at leisure, and the characteristic properties of which we can determine accurately. By the production of condensed gases an entirely new group of bodies has entered our field of vision. Our next object is plainly to find out all that we can about them. Ten years after the discovery of liquid oxygen, Olszewski had liquefied several cubic centimetres of all gases known at the time except hydrogen, had determined their boiling points with considerable accuracy as well as their critical temperatures and pressures, had solidified all except oxygen and measured their triple points, had measured the densities of the liquefied gases boiling under atmospheric pressure and had even observed the absorption spectrum of liquid oxygen. It is true that none of Olszewski's determinations has survived the intervening half-century, but in all cases a repetition of his experiments under the more congenial conditions of to-day has led only to a slight correction as a result of greater accuracy in the measurement of temperature and pressure and greater

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purity of the material investigated. In 1887 Olszewski knew almost as much about liquefied gases as we know to-day. When we remember that the era of commercial gases had not yet begun, that there were no Dewar vessels and no high vacuum pumps, we can but admire the work of the Polish scientists, carried out in a provincial university far away from the centres of learning of their time.

A short survey of Olszewski's early apparatus may serve as an introduction to low-temperature experimental technique and to the more highly developed appurtenances of the Leiden Laboratory. One of the most successful innovations of the Polish school was the introduction of liquid ethylene as a cooling agent. The advantage of this substance is that it may be liquefied slightly below room temperature at moderate pressure, whereas a vapour pressure of 10 mm. of mercury corresponds to a temperature of -150°C . This temperature is well below the critical temperatures of oxygen, carbon monoxide and nitrogen, so that all these gases may be liquefied in liquid ethylene by simple compression, without employing Cailletet's expansion principle. However, in order to study them at atmospheric pressure and below, at still lower temperatures, it was necessary to devise some method of isolating them from the surrounding ethylene cryostat. This was accomplished with considerable success, as shown in fig. 1. Olszewski kept his liquid ethylene in a steel flask containing a syphon and immersed in a bath of ice and salt. Under these conditions the vapour pressure of ethylene is 32 atm. The liquid then passed through a copper spiral contained in a bath of CO_2 and ether, the vapour pressure of which was reduced by a vacuum pump so as to give a temperature of about -100°C . Through this spiral the ethylene was expanded to atmospheric pressure into a glass vessel *g*. Part of the ethylene naturally evaporated on expansion, but by keeping the CO_2 vessel sufficiently cold, 230 grm. of ethylene could be made to give 150 c.c. of liquid in a glass vessel at atmospheric pressure, i.e. at a temperature of -104°C . This was sufficient for a number of experiments.

Inside the glass vessel *g* were placed a number of concentric glass tubes *t* closed at the bottom, into the innermost of which

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the liquid ethylene was introduced. Thus, when the vapour pressures were further lowered by pumping through *n*, the cold ethylene vapour passing round the intervening glass tubes served to shield the liquid from the warm air of the atmosphere. This protection, together with that offered by the concentric glass walls, proved sufficient to keep the liquid ethylene at 10 mm. C_2H_4 pressure for a considerable time.

Olszewski's actual experiments with liquid gases were carried out inside a thick-walled glass tube *a*, immersed in the liquid ethylene and sealed to a brass cap *c* traversed by two narrow metal tubes. One of these was connected to a hydrogen gas-thermometer vessel *h* inside *a*, the other to a metal flask containing at high pressure the gas to be liquefied. To the glass tube *a*, which was 30 cm. long and had an inner diameter of 14 mm. and walls 3.5 mm. thick, Olszewski devoted great attention. By very carefully annealing the tube he was able to apply pressures of 60 atm. for long periods as well as sudden changes of temperature. In order to study the condensed gases at atmospheric pressure and below, the tube *a* contained yet another tube *u* closed at the bottom. The gas first condensed in the outer annular space between *a* and *u*, then rose to the top of *u* and flowed over. When the vapour pressure was reduced the liquid naturally evaporated first from the annular space, which through the glass wall of *a* was in contact with the liquid ethylene. The liquid in the innermost tube was thus shielded from the liquid ethylene by a cylinder of gas at low pressure as well as two glass walls. The insulation, which

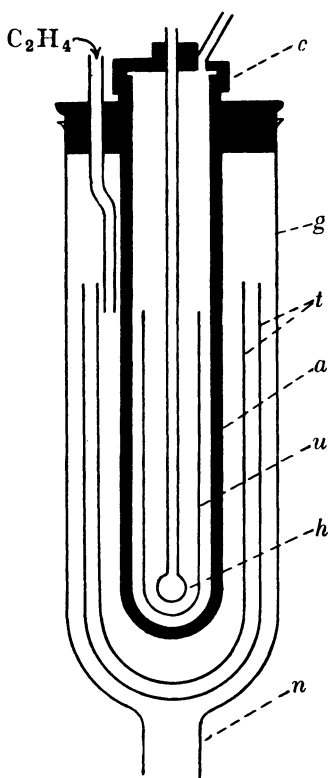


Fig. 1. Olszewski's apparatus for experiments with liquefied gases.

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appears primitive enough to-day, enabled Olszewski to pump off solid nitrogen well below the triple point, reaching a minimum temperature of -225°C. , as read on his hydrogen thermometer. A careful study of Olszewski's papers will show that the accuracy of his temperature determinations in this region was probably better than $\pm 2^{\circ}$. -224°C. is still the lowest temperature that we can hope to reach with solid nitrogen without employing very complicated methods.

One of Olszewski's first experiments was to combine his refrigerating system with an expansion device according to Cailletet for the purpose of liquefying hydrogen. A narrow glass tube filled with gaseous hydrogen, capable of withstanding 200 atm., was bent twice at right angles. One end was immersed in liquid nitrogen, the other connected to a mercury pump as in Cailletet's experiments. When the mercury pressure was suddenly released, a fog of liquid hydrogen was observed in the tube, which was immediately obliterated by a fog of solid nitrogen. But Olszewski was unable by this method to obtain liquid hydrogen "boiling quietly in a test-tube". The liquid hydrogen evaporated as soon as it was formed, and its production in sufficient quantities to enable measurements to be made was the outcome of a new principle which will be discussed in the next chapter.

It may appear unfair to Olszewski, whose experiments were continued with great success until well into the present century, to break off at this point our description of his work. Yet towards the end of the nineties the Crakow school fell into the shadow of new developments originating in other countries, and before the close of the century the centre of gravity of low-temperature research had shifted definitely to Holland.

I. I. 3. *Van der Waals' Equation and the Law of Corresponding States*

With the help of concepts developed in the kinetic theory of gases van der Waals in 1873 introduced his well-known equation of state. Assuming the molecules of a gas to occupy a finite volume and to exercise well-defined forces on one another, he thus gave the first hypothesis concerning the laws of inter-

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action of material particles. However summary and incomplete this picture of a molecule must necessarily be, van der Waals' equation has been extraordinarily successful in describing qualitatively and to a certain extent quantitatively the properties of real and condensed gases. Half a century elapsed before quantum mechanics in the hands of London gave a more detailed and comprehensive account of the nature of van der Waals' forces.

Writing van der Waals' equation in the form

$$(p + a/v^2)(v - b) = RT,$$

we shall develop as briefly as possible the consequences to which it leads us.

The equation being cubic in v , we see at once that the isothermal curves will in general have a maximum and a minimum, which may or may not be real. It is hardly necessary to show how these maxima and minima may be superposed on Andrews' isothermals, giving the unstable and metastable homogeneous states, which may exist apart from the stable two-phase condition. The laws of thermodynamics show that Andrews' horizontal straight lines, marking the states of liquid vapour equilibrium, must be so situated that the closed areas cut off in van der Waals' curves above and below these lines are equal to one another. The equation, which contains the three constants a , b and R , enables us to compute the critical temperature, pressure and volume as a function of these constants. Indeed the critical point, which we know to be given by a horizontal point of inflexion, can be expressed mathematically by setting the first two derivatives of p by v equal to zero. This leads to two new equations:

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT_c}{(v_c - b)^2} + \frac{2a}{v_c^3} = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{2RT_c}{(v_c - b)^3} - \frac{6a}{v_c^4} = 0,$$

which, together with the equation of state itself, are sufficient to compute T_c , v_c and p_c as functions of a , b and R . The result is

$$T_c = 8a/27bR, \quad v_c = 3b, \quad p_c = a/27b^2.$$

Similarly, R , a and b may be derived from the critical constants