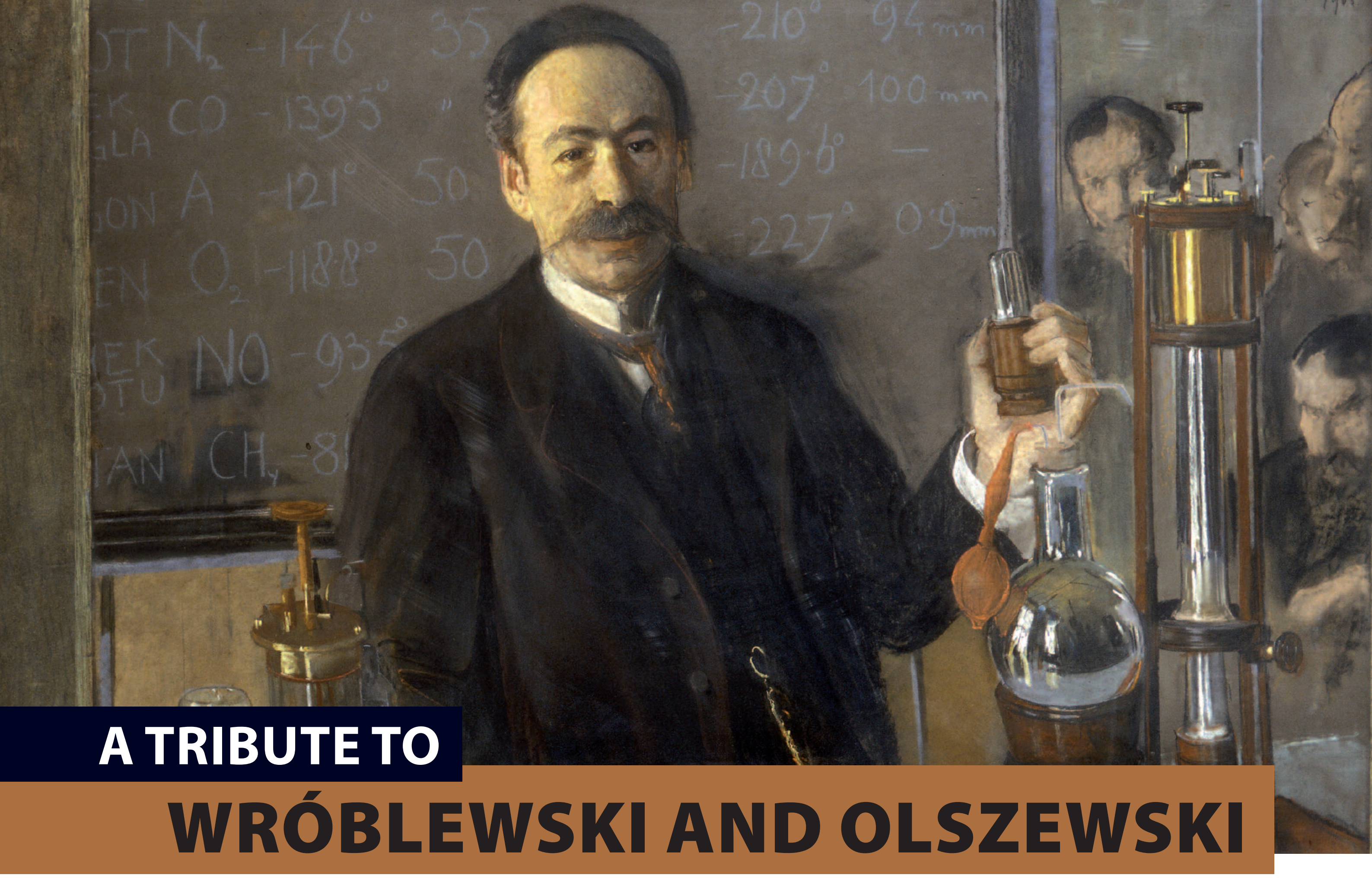

▲ Painting of Olszewski at work, with some of his equipment (by J. Wynosz, 1905).

A TRIBUTE TO WRÓBLEWSKI AND OLSZEWSKI

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DOI: 10.1051/epn/2010402

Poland still vividly remembers its era of greatness. These were the days of Mikolaj Kopernik and his later followers Jan Brozek, the mathematician, and Stanislaw Pudlowski, who, in 1640, met Galileo at Arcetri. More recently Zygmunt von Wróblewski (1845-1888) and Karol Olszewski (1846-1915) acquired continental standing through their liquefaction achievements.

Zygmunt von Wróblewski was born in Grodno, Lithuania, as the son of a lawyer. His academic studies, at the University of Kiev, were interrupted in 1862 after the January Revolution in Poland: because of his participation, Wróblewski was bannished to Siberia. In 1869 he was amnestied and allowed to study successively in Berlin and Heidelberg; in Munich he passed the PhD (1874). Through a stipend of the Cracow Academy of Sciences, Poland's oldest scientific institution, Wróblewski made a grand European tour, visiting Strasbourg, Paris, London, Oxford and Cambridge. In September 1882 he was nominated at Cracow's Jagiellonian University as head of the Physics Department. At Paris he had made the acquaintance of Louis Paul Cailletet in the latter's laboratory, where the liquefaction of gases, one of the major themes of 19th century physics, determined the agenda. With the support of Olszewski, Wróblewski launched a programme of his own, with apparatus brought with him from France.

Karol Olszewski was a native from Broniszow, Poland, who studied at the universities of Cracow and Heidelberg; at Heidelberg he had earned a PhD in chemistry (1872). At his *alma mater*, he became the assistant of the chemist Emil Czyrnianski. In this position he made the acquaintance of Wróblewski, on the latter's arrival. Czyrnianski was kind enough to allow his assistant to join forces with the newcomer, if only because of the latter's cutting edge instruments.

Liquefaction fever

Early in the 19th century the age-old molecular theory had been generalized by Laplace in the framework of the brand-new doctrine of three states of aggregation and its corollary, the theory of heat. Each and every substance was expected to have a melting and a boiling point and, depending on the atmospheric pressure, to be capable of passing through the three states. New substances challenged both chemists and physicists. One of these was a yellow solid that emerged when (wet) chlorine gas was


▶ FIG. 1: Aquarel of Zygmunt von Wróblewski by H. Wdowiszewski (around 1884).

cooled down. For a while it was thought to be *solid* chlorine. In 1823, Michael Faraday established its nature and composition: chlorine hydrate ($Cl_2.10H_2O$). He put a sample in a bent tube, sealed it carefully and heated it. The result was a double layer of liquids, the lowest being deep yellow: apparently liquid chlorine. The cooling agents of the time were ice-salt mixtures, which, depending on the salt, reached at best about minus 50 degrees Celsius. This was not particularly impressive, given the existence of an absolute zero of temperature, at minus 266,66 degrees on the same scale, as calculated by Clement and Desormes (1819). High pressures as such were hard to realize for the time being. The *in situ* production by chemical reactions of high pressured gases, then, was an attractive alternative. So Faraday succeeded in producing liquid carbonic acid by putting concentrated sulphuric acid and ammonium-carbonate in the two legs of a bent tube. After sealing it, he mixed the reagents by shaking and noticed again a two-layers' system of liquids. The reaction mixture could, of course, also be subjected to cooling with ice-salt, but in this case the cooling was without avail. Further progress had to wait for the 1840's when Charles Saint-Ange Thilorier discovered a new, truly ground-breaking cooling agent, namely *solid* carbonic acid in liquid ether, capable of attaining -110 °C. 'Thilorier's mixture' became a revelation in the hands of Faraday. The experiments were not harmless, to say the least, as Faraday repeatedly experienced himself.


▶ FIG. 2: Self-photograph on sepia-paper of Karol Olszewski (around 1884).

In the summer of 1822, Cagniard de la Tour (Paris) had observed something peculiar outside mainstream physics. When a sealed tube filled with ether for about half its volume was heated, *all* of the liquid passed into the gaseous state, notwithstanding the huge pressure of 37-38 atmospheres. The temperature was about 200 °C. The Cagniard phenomena were reconsidered by the Russian chemist Mendeleev in 1859-1861 during a stay at Heidelberg, while studying the dilatation of liquids above their boiling points in sealed tubes. There was a particular temperature at which that cohesion was expected to vanish, just like the latent heat of evaporation. For ether that temperature would be about 190 °C. Mendeleev called it the 'absolute boiling point'.

Early in 1861, Thomas Andrews (Belfast) set out to focus on carbonic acid and air. His results appeared in print only in 1869 under the title 'On the continuity of the gaseous and liquid states of matter'. This seminal paper contains the notion of a substance's 'critical temperature'. James Thomson and Johan van der Waals were to elaborate on it. In the early 1870's it was recognized, then, within the framework of the kinetic theory, that each substance was characterized by a particular temperature at which the liquid continuously changed into a vapour, and *vice versa*, as if there were no longer latent heat involved.

The 'dynamic' and 'static' states of a liquid

On 24 December 1877 the Paris *académiciens* heard of two major innovations concerning oxygen. One of the communications–cabled two days before from Switzerland–came from Raoul-Pierre Pictet (1846-1929) of the University of Geneva. Pictet was a cryogenic expert who had used his expertise for the construction of artificial ice skating rinks. He announced the production of a jet of liquid oxygen. His technique implied the stepwise cooling of high pressured oxygen gas, freshly prepared by pyrolysis of potassium chlorate ($KClO_4$). The oxygen produced was at a pressure of 320 atmosphere and once at -140 °C, it was allowed to suddenly expand by opening a cock. A jet of liquid oxygen escaped, the remaining part being further cooled. In all this, Mendeleev's 'absolute boiling point' or Andrews' 'critical temperature' did not play any role at all.

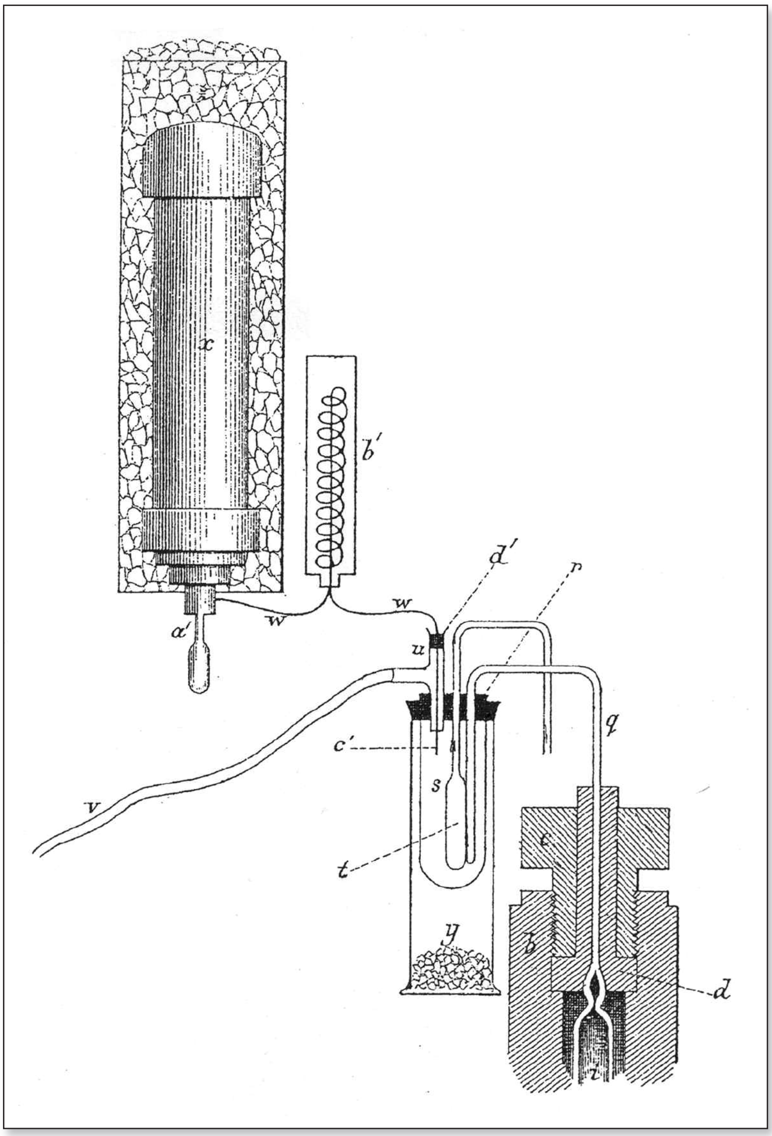
At the same meeting of the Academy a paper by Louis-Paul Cailletet announced a similar result. His approach consisted in applying huge pressures, followed by a sudden release. Without paying attention to the theoretical context–just like Pictet– he successively worked on acetylene, nitrogen dioxide, oxygen, and nitrogen. In all these cases he noticed not so much a liquid with a meniscus but a dense fog, that is, the 'dynamic' state as it was called, very close to the liquefaction point. Hydrogen was also tried out, but did not show any 'dynamics' if released at -28° and 300 atm. Later, however, 280 atm was sufficient to produce for a short while a very subtle mist. Cailletet's compression pumps and his manometers were wonders of the day.

Wróblewski and Olszewski: liquid oxygen in the *static* state (1883)

Cailletet's instrument, at the Ecole normale supérieure of Paris, had been studied carefully by at least one of his visitors: Zygmunt von Wróblewski. Upon returning to Poland, the latter brought with him an enlarged copy of it, made in Cailletet's workshop, and able to handle 200 cc of gas. Already in 1883 a first joint paper with Olszewski appeared: 'Ueber die Verflüssigung des Sauerstoffs, Stickstoffs und Kohlenoxyds', in *Wiedemann's Annalen der Physik* [1]. The gases were compressed by a force pump with mercury as an intermediate: the pump consisted of a piston in a barrel actuated by a screw which was driven by a huge wheel. Liquid ethylene, pre-cooled by a mixture of solid carbonic acid and ether, was used as a refrigerator. A hydrogen thermometer allowed one to follow the temperature (Figure 3).

The results were impressive: on April 4th, 1883, oxygen, for instance, showed up at -130 °C in a glass capillary tube as a colourless liquid [2] when the pressure was about 20 atm. By reducing the pressure it could be made to boil. This was, properly speaking, the real 'static' state. On a weekly base Wróblewski and Olszewski subsequently cabled their results to Paris where they appeared in the *Comptes Rendus* of the Academy. Oxygen was followed by nitrogen and carbon monoxide; hydrogen was next put on trial but did not give way, not even at -136 °C and 150 atm. The liquid oxygen, if it was indeed perceptible, could not yet be handled separately, however–let's say, poured from one flask into another– so there was still work to do.

By subtly varying the quantity of liquid Wróblewski and Olszewski were able to change its temperature. Indeed, when part of the liquid was above the boiling ethylene its temperature slightly rose and, with it, the pressure. At some point, the meniscus appeared to flatten and even to disappear. By lowering the mechanical pressure, the meniscus returned. Wróblewski–working alone now–noticed that the critical phenomena showed up at one particular pressure: about 50 atm. The critical temperature was far more difficult to determine. However, by adapting the pressure on the liquid ethylene its temperature could be made to vary



▲ **FIG. 3:** The refrigerating part of Wróblewski and Olszewski's liquefactor. The glass cylinder is closed with an airtight perforated rubber stopper, *r*, and contains calcium chloride, *y*, to eliminate water vapour. The round bottomed vessel *s* in it features the hydrogen thermometer *t*, the liquid ethylene inlet *c'* and the closed capillary with the oxygen, *q*. On the lower right the (modified) Cailletet compressor is shown only partly; i is the container with 200 cm^3 oxygen, to be compressed by a screw driven piston carrying mercury. The liquid ethylene is kept at *x* under and an ice-salt mixture (-20 °C); *a'* is a cock; it enters through a copper tube *ww*–partly spiralized to allow for further cooling by a 'Thilorier mixture' (ether and solid carbonic acid; *b'*)–fixed with a second stopper through a T-piece (*d'*). Tube *v* (lead) is linked to a vacuum pump, to make the ethylene boil at wish (lowest temperature attained -136 °C, at 2,5 cm Hg). Through the liquid ethylene the liquefied oxygen may be observed, if needed by using a beam of light (from ref. [1]).

▲ **FIG. 4:** The sealed flasks with argon (300 cm³) and helium (ca. 140 cm³) as sent by William Ramsay to Olszewski on 24 December 1894 and in July 1895, respectively.

considerably, which enabled one to follow the whereabouts of the meniscus. In this way, Wróblewski arrived at an estimate of -113 °C. Instead of the hydrogen thermometer a new, electric device was also tested (1885). It was a variant of the bolometer, based on the temperature dependency of the resistance of metals. In this context Wróblewski noticed that the resistance of copper in liquid nitrogen tended to zero. A sensational find, indeed, which made colleagues openly speculate on its potentialities. About 1886 and for unknown reasons Wróblewski changed the topic of his research. He tragically died, in his early forties, after a fire in the laboratory. Olszewski, already working on his own since late 1883, continued what came to be known as the Polish tradition in liquefaction.

Europe in the making: Ramsay and Olszewski (1895)

As is perfectly understandable in such a high-profile research domain, some rivalry arose, opposing Olszewski to James Dewar. Dewar had made fascinating discoveries on his own account, but tended to claim more than his fair share. It was the time that some *British* physicists openly complained about *British* colleagues who tended to deny honours due to foreigners. So it came, doubtless, that William Ramsay did *not* ask Dewar–working around the corner in London–to try to liquefy his newly discovered 'argon' and 'helium', but instead sent samples to Olszewski in Cracow (Figure 4). Argon did yield, indeed; it liquefied at -187,0 °C, solidified at -189,6 °C, with T_{crit} = -121 °C and p_{crit} = 50,6 atm [3]. Helium did not give way. ■

Acknowledgment:

The author is indebted to the Polish Academy of Arts and Sciences, Cracow, personified by Andrzej Wróblewski, vice-President, and the Museum of the Jagiellonian University (Cracow; courtesy photographs).

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Notes & references

See particularly T. O'Conor Sloane, *Liquid air and the liquefaction of gases*, London: Sampson Low, Marston & Co., 1899 and J. Rafalowiz, 'History of cryogenics in Poland', in: R.-G. Scurlock (ed.), *History and origins of cryogenics*, Oxford: Clarendon Press, 1992, p.101-121.

[1] Z.Wróblewski and C. Olszewski, *Wiedemann's Annalen der Physik* **20** (1883) 243

[2] The quantity was apparently too small to see the blueish colour.

[3] C. Olszewski, *Nature* **51** (1895) 355