contain a large number of Chinese novelties. One part of the last volume is devoted to the Stapeliæ of South Africa. The seventeenth volume is wholly devoted to new ferns; and the first volume of what it is intended to call the fourth series will consist entirely of orchids. Three parts of this have already appeared.

ON VAN DER WAALS'S TREATMENT OF LAPLACE'S PRESSURE IN THE VIRIAL EQUATION: A LETTER TO PROF. TAIT.

MY DEAR PROF. TAIT,—In Part IV. of your "Foundations of the Kinetic Theory of Gases,"[1] you take exception to the manner in which Van der Waals has introduced Laplace's intrinsic pressure K into the equation of virial. "I do not profess to be able fully to comprehend the arguments by which Van der Waals attempts to justify the mode in which he obtains the above equation. Their nature is somewhat as follows:—He repeats a good deal of Laplace's capillary work, in which the existence of a large, but unknown, internal molecular pressure is established, entirely from a statical point of view. He then gives reasons (which seem, on the whole, satisfactory from this point of view) for assuming that the magnitude of this force is as the square of the density of the aggregate of particles considered. But his justification of the introduction of the term a/v^2 into an account already closed, as it were, escapes me. He seems to treat the surface-skin of the group of particles as if it were an additional bounding-surface, exerting an additional and enormous pressure on the contents. Even were this justifiable, nothing could justify the multiplying of this term by $(v - \beta)$ instead of by v alone. But the whole procedure is erroneous. If one begins with the virial equation, one must keep strictly to the assumptions made in obtaining it, and consequently *everything* connected with molecular force, whether of attraction or of elastic resistance, must be extracted from the term $\Sigma(Rr)$."

With the last sentence all will agree; but it seemed to me when I first read Van der Waals's essay that his treatment of Laplace's pressure was satisfactory, and on reperusal it still appears to me to conform to the requirements above laid down. As the point is of importance, it may be well to examine it somewhat closely. The question is as to the effect in the virial equation of a mutual attraction between the parts of the fluid, whose range is small compared with the dimensions of bodies, but large in comparison with molecular distances.

The problem thus presented may be attacked in two ways. The first, to which I will recur, is that followed by Van der Waals; but the second is more immediately connected with that form of the equation which you had in view in the passage above quoted.

In the notation of Van der Waals (equation 8)

$$\tfrac{1}{2}\Sigma mV^2 = \tfrac{1}{2}\Sigma f\rho - \tfrac{1}{2}\Sigma Rr\cos(R, r),$$

where V denotes the velocity of a particle m, which is situated at a distance r from the origin, and is acted upon by a force R, while (R, r) denotes the angle between the directions of R and r. The intermediate term is to be omitted if R be the total force acting upon m. It represents the effect of such forces, f, as act mutually between two particles at distances from one another equal to ρ. In the summation the force between two particles is to be reckoned once only, and the forces accounted for in the second term are, of course, to be excluded in the third term.

In the present application we will suppose all the mutual forces accounted for in the second term, and that the only external forces operative are due to the pressure of the containing vessel. No one disputes that the effect of the external pressure is given by

$$-\tfrac{1}{2}\Sigma Rr\cos(R, r) = \tfrac{3}{2}pv;$$

so that

$$\tfrac{1}{2}\Sigma mV^2 = \tfrac{3}{2}pv + \tfrac{1}{2}\Sigma\rho\phi(\rho),$$

if with Laplace we represent by $\phi(\rho)$ the force between two particles at distance ρ. The last term is now easily reckoned upon Laplace's principles. For one particle in the interior we have

$$\tfrac{1}{2}\cdot 4\pi\int_0^\infty \phi(\rho)\rho^3 d\rho,$$

and this, as Laplace showed,[1] is equal to 3K. The second summation over the volume gives $3Kv$, but this must be halved. Otherwise each force would be reckoned twice. Hence

$$\tfrac{1}{2}\Sigma mV^2 = \tfrac{3}{2}pv + \tfrac{3}{2}Kv = \tfrac{3}{2}v(p + K),$$

showing that the effect of such forces as Laplace supposed to operate is represented by the addition to p, the pressure exerted by the walls of the vessel, of the intrinsic pressure K. In the above process the particles situated near the surface are legitimately neglected in comparison with those in the interior.

Van der Waals's own process starts from the original form of the virial equation—

$$\tfrac{1}{2}\Sigma mV^2 = -\tfrac{1}{2}\Sigma Rr\cos(R, r),$$

where R now refers to the *whole* force operative upon any particle; and it appears to me equally legitimate. For all particles in the interior of the fluid R vanishes in virtue of the symmetry, so that the reckoning is limited to a surface stratum whose thickness is equal to the range of the forces. Upon this stratum act normally both the pressure of the vessel and the attraction of the interior fluid. The integrated effect of the latter throughout the stratum is equal to the intrinsic pressure, and, on account of the thinness of the stratum, it enters into the equations in precisely the same way as the external pressure exerted by the vessel. The effect of Laplace's forces is thus represented by adding K to p, in accordance with the assertion of Van der Waals.

I am in hopes that, upon reconsideration, you will be able to admit that this conclusion is correct. Otherwise, I shall wish to hear more fully the nature of your objection, as the matter is of such importance that it ought not longer to remain in doubt.

Believe me yours very truly,

RAYLEIGH.

L'Abbaye de St. Jacut-de-la-Mer, September 7.

[1] Ed. Trans., vol. xxxvi., Part 2, p. 261.

[1] See also *Phil. Mag.*, October 1890, p. 292.

NOTES.

THE French Association for the Advancement of Science met at Marseilles on September 17, under the presidency of M. P. P. Dehérain, who chose as the subject of his address the part played by chemistry and physiology in agriculture. The meeting comes to an end to-day. There were general excursions on Sunday to Arles, and on Tuesday to Aix; and it is proposed that to-morrow, the 25th, there shall be a final excursion to the Mediterranean coast.

THE Congress of German Naturalists and Physicians was opened at Halle on Monday by Prof. His, of Leipzig. The meeting was attended by 1215 persons, including many distinguished foreign physicians and men of science and 280 ladies.

THE Helmholtz celebration, deferred from August 31, is now fixed for November 2. After the ceremony the delegates and others will dine together at the Hotel Kaiserhof.