of voyages of discovery made during antiquity and the middle ages, as far as Magellan's first voyage round the globe, will be shortly published by Herr Spamer of Leipzig. It will contain some 100 illustrations, besides maps, charts, &c.

CRITICAL TEMPERATURE OF ETHYLENE

M. AMAGAT (*Compt. rend.*,¹ [1879], lxxxix, p. 437, corrected *Beiblätter* [1880], iv, p. 19) has submitted hydrogen, oxygen, nitrogen, air, carbon monoxide, methane, and ethylene at temperatures from 18° to 22° to pressures ranging between 28 and 431 atmospheres, and finds that, except for hydrogen, the product $p\bar{v}$ first diminishes and then increases as p increases, the most marked case being that of ethylene, for which the values of $p\bar{v}$ at 31·58, 84·16, 398·71 atmospheres are proportional to 2·29, 1, 3·13 respectively. Dr. van der Waals deduced this general peculiarity theoretically in 1873, and showed that its markedness is the greater, the less the temperature of compression exceeds the critical temperature: concluding, therefore, that for ethylene the critical temperature is not far below 18°, as M. Amagat has also surmised, he has recently (*Meded. der k. Akad. van Wetenschappen in Amsterdam*, Mei 1880)² determined it directly by a Cailletet compression-apparatus, finding it to be 9°·2, and the critical pressure 58 atmospheres.

On p. 55 of his dissertation "Over de Continuïteit van den Gas- en Vloeistoftoestand" (Leiden, 1873), van der Waals finds the characteristic equation of a gas in the form—

$$\left(p + \frac{a}{v^2}\right)(v - b) = R(1 + \alpha t),$$

where a, b, R are constants and α the coefficient of expansion, and on p. 79 *et seq.* it is shown that at the critical temperature all three values of v given by this equation, which may be written

$$v^3 - \left\{b + \frac{R(1 + \alpha t)}{p}\right\}v^2 + \frac{a}{p}v - \frac{ab}{p} = 0,$$

are equal: hence, if V is put for this common value of v , and T, P for the corresponding values of t, p , *i.e.* for the critical temperature and pressure, the theory of equations gives

$$3V = b + \frac{R(1 + \alpha T)}{P}, \quad 3V^2 = \frac{a}{P}, \quad V^3 = \frac{ab}{P},$$

whence

$$P = \frac{a}{27b^2}, \quad V = 3b, \quad PV = \frac{a}{9b}, \quad 1 + \alpha T = \frac{8a}{27bR},$$

and also

$$a = 3PV^2, \quad b = \frac{1}{3}V, \quad R = \frac{8}{3} \frac{PV}{1 + \alpha T}.$$

The minimum value of $p\bar{v}$ at any temperature t may be determined in the usual way by $\frac{d(p\bar{v})}{dv}$ being equated to zero, and, if p', v' are written for the corresponding values of p, v , there result

$$v' = \frac{V}{3(1 - \tau)}, \quad p' = 27(1 - \tau)(2\tau - 1)P, \quad p'v' = 2(2\tau - 1)PV,$$

where

$$\tau^2 = \frac{bR(1 + \alpha t)}{a} = \frac{8}{27} \frac{1 + \alpha t}{1 + \alpha T}.$$

Thus a minimum value of $p\bar{v}$ exists only when

$$1 > \tau > \frac{1}{2},$$

i.e. only at temperatures that lie between

$$\frac{a}{bR\alpha} - \frac{1}{\alpha} \text{ and } \frac{a}{4bR\alpha} - \frac{1}{\alpha}.$$

If p_1 represents the pressure of the gas when occupying unit volume at t , then

$$(p_1 + a)(1 - b) = R(1 + \alpha t),$$

and, p_1 being the value of $p\bar{v}$ in this initial state, the markedness of the minimum value of $p\bar{v}$ is greater the less

$$\frac{p'v'}{p_1} \text{ or its equivalent } \frac{(1 - b)(2\tau - 1)}{\tau^2 - b(1 - \tau)},$$

that is, since the sign of the t -differential coefficient of this expression is the same as that of $(\tau - b)(1 - b - \tau)$, the less t , provided that

$$1 - b > \tau > b,$$

¹ Since the following was written, M. Amagat has published further results, which do not however affect its main point.

² Mr. Dickson seems to have independently discovered (*Phil. Mag.* for July, 1880) the principles laid down by Dr. van der Waals in his above mentioned dissertation, pp. 79-93, which is not sufficiently known in England

or that the temperatures lie between

$$\frac{a(1 - b)^2}{bRa} - \frac{1}{\alpha} \text{ and } \frac{ab}{Ra} - \frac{1}{\alpha}.$$

If v represents the volume of the mass of gas which occupies unit volume at 0° under unit pressure, then

$$R = (1 + a)(1 - b),$$

as is taken in the following calculations.

In the case of ethylene van der Waals' experiments give $T = 9\cdot2$ and $P = 58$: hence, by the above relations with $a = 0\cdot00367$,

$$\frac{a}{b(1 + a)(1 - b)} = 3\cdot489, \quad \frac{a}{b^2} = 1566,$$

which lead to a cubic equation that gives

$$a = 0\cdot00786, \quad b = 0\cdot00224, \quad R = 1\cdot0056,$$

so that the characteristic equation is

$$p = \frac{0\cdot0037(272\cdot5 + t)}{v - 0\cdot00224} - \frac{0\cdot00786}{v^2},$$

the pressure being reckoned in atmospheres; hence too $V = 0\cdot0067$ and $PV = 0\cdot39$. Further, when $t = 20$, the mean temperature in Amagat's experiments, $\tau = 0\cdot5547$, and thus by calculation $p' = 76\cdot25$, while Amagat's direct observations give $p' = 84$ approximately, so far justifying the theory. The temperatures for which $p\bar{v}$ has a minimum value range from 678° to -35°.

The intimate agreement between Amagat's experiments and van der Waals' formula (which is entirely independent of them) is shown by the following table, wherein the first column contains the pressures (expressed in atmospheres) employed by Amagat, the second his experimental values of $p\bar{v}$ divided by 23500, and the third the values of $p\bar{v}$ calculated for $t = 20$ from the formula:—

p	$p\bar{v}$ observed.	$p\bar{v}$ calculated.
31·58	0·914	0·895
45·80	0·781	0·782
59·38	0·522*	0·624
72·86	0·416	0·387
84·16	0·399	0·392
94·53	0·413	0·414
110·47	0·454	0·456
133·26	0·520	0·520
176·01	0·643	0·642
233·58	0·807	0·805
282·21	0·941	0·940
329·14	1·067	1·067
398·71	1·248	1·254

The only serious discrepancy occurs for $p = 59\cdot38$, and van der Waals accounts for this by supposing that in Amagat's table 12263 is misprinted for 15263, so that the asterisked number should be 0·650; for by experiment he finds that the ratio of the values of $p\bar{v}$ for $p = 45\cdot80$ and $p = 59\cdot38$ is 1·26 (the calculated ratio being 1·25), while Amagat's actual numbers give 1·50, but, when corrected, 1·20.

For methane the equation of van der Waals' form that best satisfies Amagat's experimental values has for constants $a = 10^6 \times 2\cdot9$, $b = 53$, $R = 25525$, if $t = 20$, $a = 0\cdot00367$, pressures being measured in metres of mercury, and this gives $-99\frac{1}{2}$ for the critical temperature and $50\frac{1}{2}$ atmospheres for the critical pressure. The constants have large values here, for, as calculation shows, the mass of the gas considered is about $24\frac{1}{2}$ grams, which would occupy, at 0° under one atmosphere, about 33518 c.c.

This discussion—with the numbers recalculated—by Dr. van der Waals of M. Amagat's experiments in connection with the critical temperature is here reproduced, together with the brief *résumé* of his theory (which has not hitherto appeared in an English dress), for ready application in other cases.

September 17

ROBERT E. BAYNES

UNIVERSITY AND EDUCATIONAL INTELLIGENCE

CAMBRIDGE.—The Natural Science Tripos Class List has just been issued. There are eight names in the first class, eight in the second, and fifteen in the third. Of those in the first class three attain their first class for Physics and Chemistry, viz.: Fleming, St. John's (distinguished in Physics); S. L. Hart, St. John's, and Heycock, King's. Two attain their first class for