

which, like ethylene, carbonic acid, and the protoxide of azote, have their critical points at ordinary temperatures. These are the bodies that I propose to investigate, and with the Academy's permission, I will communicate to it the results of my researches on this subject.*

ON THE HEAT OF VAPORIZATION OF LIQUID CARBONIC ACID NEAR ITS CRITICAL POINT.

By E. MATHIAS.†

[Translated by Chief Engineer ISHERWOOD, U.S.N.]

In a preceding note‡ I described a method of measuring, *at constant temperature*, the heat of vaporization of liquefied gases, the source of the compensating heat being the heat of dilution of sulphuric acid in the water of the calorimeter.

I have applied this method without modification to sulphurous acid, to carbonic acid, and to the protoxide of nitrogen, within the limits of the atmospheric temperatures of the room in which I operated ($+ 25^{\circ}$ to $+ 22^{\circ}$).

In order to operate between $+ 22^{\circ}$ and the critical point ($+ 31^{\circ}$) of carbonic acid, the method was modified in the following manner:

By means of a suitable system of burning gas jets fitted with regulators, I raised the temperature of the operating-room a little above the temperature *t*^o at which I wished to experiment, and I maintained this raised temperature constant. I then filled the outer space of the Berthelot calorimeter with water of the same temperature, and, finally, I filled the calorimeter with water at *t*^o, and closed it by a cover through which the vertical tube from the reservoir of the liquefied gas passed. A sensitive thermometer showed

* The work has been done in the laboratory of the physical school at the Sorbonne.

† *Comptes Rendus*, 1889, p. 470.

‡ *Comptes Rendus*, 1889, p. 1146.

the temperature of the water in the calorimeter and of the liquefied gas in the reservoir. There was then established between the air of the room, the outer space of the calorimeter, and the calorimeter itself, an equilibrium such that, if all the conditions were adroitly adjusted, the temperature of the calorimeter would vary with extreme slowness. With a little experience the water of the calorimeter could be brought within 0.05° of the t° and maintained there. Under these conditions, I raised the cover of the calorimeter and proceeded with the experiment as at ordinary temperatures to that near which the rapidity of cooling is a little greater. The sole inconvenience of this method is that the experimenter is obliged to be under the temperature t° of the experiment.

Denoting by P' the diminution of the weight of the reservoir of the liquefied gas, the weight P of the liquid vaporized at t° is given, as has been shown* by the formula

$$P = P' \frac{\delta}{\delta - \delta'}$$

δ and δ' being the densities of the liquid and of its saturated vapor at t° .

In the neighborhood of the critical point, the coefficient $\frac{\delta}{\delta - \delta'}$ has very large values, and the weight P of the gas which passes off should be more and more lessened in order to prevent too great a discharge and consequently expansion.†

As the liquefied gases, although prepared with the

* J. Chappuis, *Comptes Rendus*, 1887, p. 897.

† It will be sufficient to discharge the gas in the Bourdon manometer which indicates the pressure, the second cock being closed and inoperative. Previous experiments gave the weight of gas corresponding to the indications of the manometer. The weight of liquid vaporized can thus be exactly regulated. In order to avoid expansion, I generally limited myself in the definite experiments to the vaporization of only the weight of liquid comprised between $\frac{1}{4}$ and $\frac{1}{2}$ gram per minute (discharge = 15 to 20 minutes). There are thus developed but small quantities of heat, and the interior cooling of the apparatus, which is difficult of measurement in the case of high pressures, becomes negligible.

greatest care, always contain a little air, they have to be analyzed, and denoting by a the proportion of air thus found, the numbers ascertained for the heat of vaporization must be augmented in the ratio of a in 100.*

I have thus determined the heat of vaporization of carbonic acid with three samples of the liquid independently prepared by myself, and containing, respectively, 0.71, 2.15 and 0.76 per cent. of air.

The following are the numbers obtained, correction being made for the air:

<i>Temperature ° of the Carbonic Acid.</i>	<i>Heats of Vaporization Experimentally Determined in Calories.</i>	<i>Heats of Vaporization Calculated by Formula in Calories.</i>
6.65	50.76	51.05
12.35	44.97	45.23
16.46	39.92	40.30
22.04	31.80	32.00
26.53	22.50	22.80
28.13	19.35	18.34
29.85	14.40	11.64
30.59	7.26	7.01
30.82	3.72	4.61

The third column contains the numbers calculated by the formula—

$$L^2 = 118.485 (31 - t) - 0.4707 (31 - t)^2,$$

deduced by Messieurs Cailletet and Mathias† from the well-known formula of Clapeyron—

$$L = \frac{T}{E} (u' - u) \frac{dp}{dt}$$

and the ascertained values of u , u' and $\frac{dp}{dt}$

The accord of the numbers experimentally determined

* The heat of dissolution of the air in the liquefied gas is also neglected.

More exactly $L' = L \frac{100}{100 - a}$, L' and L being the crude, uncorrected numbers.

† Cailletet and Mathias, *Journal de Physique*, 2d series, vol. v, 1885, p. 562. The formula in L has allowed the foreseeing of the heat of vaporization at zero, which has recently been determined by Mr. Chappuis, *Comptes Rendus*, 1888, p. 1007.

and calculated by the formula is, I may say, a very satisfactory verification of the formula of Clapeyron.

If a curve be constructed having the temperatures for abscissas and the experimentally determined numbers for the ordinates, the tangent to the curve at the critical point will be found perpendicular to the axis of the abscissas, from which the conclusion would seem to be warranted that *at the critical point the latent heat is rigorously nothing, and, consequently, that at the same temperature the equality $u = u'$ is also perfectly rigorous.*

There can be drawn from the above propositions other immediate deductions, which will be given in a future memoir.

THE HOLLERITH ELECTRIC TABULATING SYSTEM.

[*Report of the Committee on Science and the Arts.*]

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HALL OF THE FRANKLIN INSTITUTE,
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The Sub-Committee of the Committee on Science and the Arts, constituted by the FRANKLIN INSTITUTE of the State of Pennsylvania, to whom was referred, for examination,

THE HOLLERITH ELECTRIC TABULATING SYSTEM,

Report that: The Hollerith Electric Tabulating System is a device by which electricity is applied to the compilation and tabulation of census and other returns of a similar nature which require summation and classification under various heads and in different groups.

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