A. VAN ELDIK. *Measurements of the capillary ascension of the liquid phase of a mixture of two substances in equilibrium with the gaseous phase.*

1. If, with a view to v. D. WAALS's theory of capillarity and in connection with his theory of the ψ-surface, we wish to measure the changes of the capillary ascension of the liquid phase of a mixture of two substances, during successive variations in composition along a connode-curve presenting a plaitpoint, as far as next to this plaitpoint, several experimental difficulties occur.

In the first place care should be taken that the mixtures to be experimented with, are not mixed, even in the smallest degree, with other substances. Indeed, the experiments concerning the ψ-surface, the plaitpoints and capillarity, made by KUENEN, DE VRIES and VERSCHAFFELT at Leiden, have sufficiently shown that it is of much importance to secure a high degree of purity, if one wishes to obtain trustworthy results from this kind of investigations.

Secondly in these measurements some conditions should be considered, the satisfying of which requires particular precautions. Indeed, in performing those measurements we must be sure, that both spaces separated by the meniscus are filled with one single phase

each; i. e. that in each of those spaces apart, the composition is everywhere the same as near the meniscus. And further it is generally necessary, in measuring the ascensions, to bring the meniscus at different heights in the capillary tube, and to renew repeatedly the liquid phase in this tube.

Now, again according to the experiments of KUENEN, it is very difficult to satisfy the first condition, and to exclude the phenomena of retardation, if the phases are not thoroughly stirred. In order to satisfy the second condition, we might support the liquid phase by a movable column of mercury. But in moving this, we should disturb the equilibrium, supposed to have been reached by stirring, if by doing so the space containing the total quantity of the substance were diminished. Hence this space should be kept constant, notwithstanding the moving of the mercury-meniscus.

Of course it is necessary to keep continually the temperature rigorously constant, in order to maintain the equilibrium.

By the arrangement of the apparatus to be described hereafter, the difficulties opposing the satisfying of the enumerated conditions were overcome, and constant values could be obtained for the ascensions, among others with mixtures of Methylchloride and Ethylene. In giving this description we suppose that we are experimenting with the said substances at a temperature a little above the temperature of the room, so that f. i. the plait of 23° for a mixture of Methylchloride and Ethylene is investigated.

2. *Experimenting-tube.* This tube is represented in

fig. II. The part, serving for measuring the ascensions is the wide glass tube B, which contains the capillary tube, centred by two narrowings. At the top B carries a piece of narrow glass tube, which ends as a capillary tube within the wider piece A, in order to prevent the particles of dust, perhaps carried along by the gas streaming in, from reaching the tube B, serving for the measurements. A serves at the same time to receive the Methylchloride which may have condensed already in the copper supplying tubes, and so may have grown impure by the contact with the copper cocks, etc.

In order to allow us to move the meniscus at liberty — which is necessary also if we wish to make a series of experiments, beginning with the same quantity of Methylchloride, because at high pressure the gas dissolves to a high degree in the liquid, causing the latter to increase considerably — B is not closed at the nether end, but provided with a reservoir C, connected along the glass tube b, the steel capillary tube c and the glass tube d_1, with the pressure-cylinder D_1, filled with mercury. The pressure of an hydraulic pump is transmitted along copper tubes filled with glycerine to the mercury in this cylinder, and so in C the mercury-meniscus may be moved at liberty. The steel capillary tube, connected to the glass tubes b and d_1 by two brass pieces e, fastened to the glass by means of sealing wax, consists of two pieces, joined by a steel cock I, which closes the experimenting-tube every time when the surface of the liquid has been raised to a suitable level; in this way any leakage of pressure-cylinder or pump

was rendered harmless. With the pressure cylinder D_1 is also connected the air-manometer M, placed in another cylinder D_3, and so the pressure, occurring in the experimenting tube, (the parameter giving the places of the phases on the connode-curve) is read. By means of the cock III the manometer may be disconnected from the remaining part of the apparatus.

The reservoir C is useful, as explained above, to secure sufficient room for the moving of the meniscus, and moreover to hasten the mixing by means of a stirring-apparatus.

For this reason in this reservoir, rather large in order to allow us always to mix the liquid phase with a sufficient quantity of the gas, a little soft-iron bar is placed, of about 6 cM. length, wholly covered with glass, in order to allow the cleaning of the tube with acids, and which is provided with two glass knobs, preventing it from adhering to the side of the glass tube, and facilitating the mixing by increasing the surface of it.

This stirring-bar is moved as in KUENEN's experiments by means of electro-magnetism.

Instead of placing the windings of the coil on the iron cylinder itself, surrounding the experimenting tube, I used a common coil K (containing about 500 windings, 7 cM. in diameter and 14 cM. long), which is moved outside the water-bath surrounding the experimenting tube, whilst within it, close round the latter, a soft-iron cylinder k is suspended to the same support as the coil K, and so may be moved simultaneously with the latter.

By this means a rather strong magnetic field is obtained along the axis of the coil, so as to enable us to apply a sufficient force on the stirring bar with a moderate current ($\pm$ 2 Amp., obtained from 2 Bunsen cells), generating but little heat in the coil In order to prevent the iron from touching the glass tube, the little iron cylinder was wholly covered with sealing wax.

The current through the coil was closed only during the stirring, which consists in moving the stirring-bar up and down through the surface of the liquid. As soon as by stirring the liquid in C together with the gas above it, the thermodynamical equilibrium of the two phases, corresponding to the given temperature and pressure, has been reached, in forcing up the mercury in C, we bring the surface of the liquid into B, and there read the height of ascension.

The condition, that the whole volume, occupied by the substance, should not be altered by moving the mercury in C is now satisfied, by moving simultaneously with the mercury meniscus in C another mercury column as much in opposite direction in the reservoir E, which is connected with the space in the experimenting tube. The reservoir E is connected with the upper end A of the observation tube B by a copper tube h and the T-piece T. Along the steel tubes f it is connected with the glass tube d_2 of the mercury cylinder D_2, from which it may be disconnected by the steel cock II.

Both parts: the experimenting tube $A.B.C.$ and the reservoir E I placed one above the other in the same water bath in order to secure as much as possible the

same temperature for the whole space filled with the mixture; to this end the T-piece T received the shape represented in fig II. In the brass piece g is soldered with silver the copper tube h, which at the nether end carries a screw-nut, to be applied on the brass screw, which is fastened with sealing wax on the tube A. In order to prevent the aperture of the leather ring from being stopped up in applying the nut on the screw, a piece of steel capillary tube ($\pm$ 1 cM. long) is put into this aperture.

A similar arrangement is made at the second branch j of the T-piece, which leads to the reservoir E.

The third branch leads to the supplying tube l, along a capillary tube and the capillary cock IV.

The inferior end of E is connected by an arrangement m of the same kind, but which, on account of the presence of mercury, has been made in steel, with the steel tubes f_1 and f_2, and the steel cock II, leading to the pressure cylinder D_2.

3. *The Moving of the Phases.* In order to enable us to give to both mercury-niveaus equal and opposite displacements, — which will allways be of use in experiments on equilibrium of phases — a compound hydraulic pump was constructed, as representend by a scheme (V) in fig. I. It consists in a strong brass cylinder, divided into two parts by a piston. These two parts are connected through the cocks V and VI, each to one of the cylinders D_1 and D_2, and so the displacement of the piston is transmitted on the mercury in C and E.

The two other taps of the pump are connected with

each other by the cocks VII and VIII, and further through the cock IX with a common hydraulic pump P (pump for testing manometers, from SCHÄFFER und BUDENBERG, who also constructed the above described apparatus). This arrangement enables us to displace both menisci either separately or simultaneously.

In order to move only the meniscus in C the cocks I, V, VII, IX are opened, VIII is shut; in order to move only the meniscus in E, II, VI, VIII, IX should be open, VII shut. The motion is then obtained by means of the hydraulic pump P. For the simultaneous motion of the two niveaus VII and VIII are shut, and I, II, V, VI are opened.

Further particulars are shown by fig III.

In order to make really equal the quantities of glycerine, displaced on both sides of the piston, the piston-rod is prolonged on both sides outside the cylinder; it passes through leather packing-rings. The piston-rod ends free at one end S_1; the other end S_2 is fastened to the frame F and follows its motion, which is obtained by turning the wheel H riveted to the screw G. By means of this weel we may give a very slow motion to the piston.

4. In order to get a suitable and sufficiently constant temperature, a warm water bath is used, as represented in fig. I.

The water, streaming through the water bath, is heated in a vessel, placed at a height of about $4\frac{1}{2}$ M., and provided with a thermoregulator. In order to cause the water to stream out of this vessel under a constant difference of level, and so with a constant velocity, the

arrangement represented in fig. IV, was made. The cock *l* supplies the funnel *L*, which communicates with the heating vessel *N*, with a little more water than streams down out of *N* after being heated. The super-

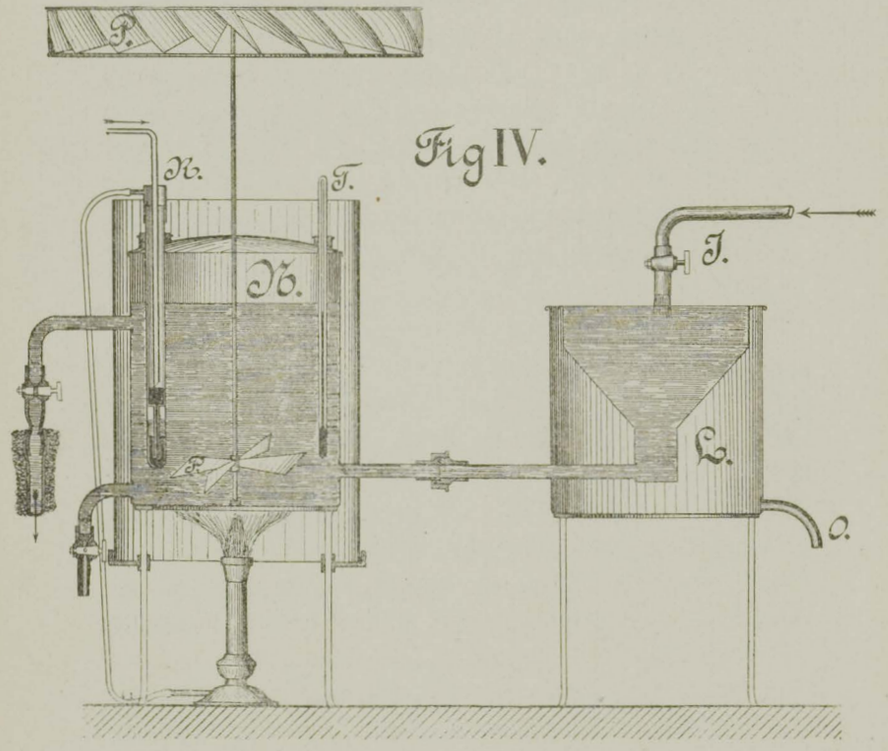


Fig IV.

fluous water flows into the vessel placed round *L*, and streams of through *O*.

Besides the thermoregulator *R* and the thermometer *f* a stirring-apparatus *P* (after the example of OSTWALD) is placed in the vessel *N*, and is made to revolve by the

heated air ascending from a Bunsen-burner. The flame placed under *N* however is not sufficient for this purpose; a second flame is wanted, placed outside the asbestos screen standing round *N*. The water heated thus streams through wool-covered tubes, and enters from above the cylindrical space between the two glass tubes, the inner of which contains the experimenting tube, and is filled with water in rest. This water is slowly heated by the warm water streaming along, and after the state of equilibrium of temperature has been reached, it renders quite imperceptible the still possible small variations of temperature. Accordingly the temperature was kept constant for hours within 0.°1; moreover it was possible to adjust it on various days exactly at the same value. As on the bursting of the experimenting tube, which occurred repeatedly, the two tubes of the water-bath were usually crushed likewise, the whole apparatus was placed in the oaken case, already described by DE VRIES. [1])

5. *Apparatus for obtaining the Mixtures.* In fig. V a scheme is given, representing the purificating apparatus, by means of which the substances, used by me, were subjected to the process of purification, indicated by KUENEN [2]). The cross-shaped copper tube *n*, connected through the cock X with the copper tube *l* leading to the experimenting tube, joins the two parts, each of which serves for one of the two components of the mixture. The piece *n* carries also the

[1]) Diss. Leid. 1893.

[2]) Arch. Néerl. 26. 1893. p. 354.

two cocks XV and XVI, one of which, leading to the mercury-air-pump, enables us to evacuate every part of the apparatus at liberty, the other serving to let escape the gas. Through the cock XI the piece n is connected with the purifying apparatus for the Methylchloride, p is the copper cylinder containing the impure liquefied gas, such as is supplied by trade; q is a strong iron tube, filled with $P_2 O_5$, and r the strong copper cylinder, in which by cooling in a mixture of solid carbonic acid and alcohol the Methylchloride is liquefied. During the distilling the cocks XII and XIV are opened, XI shut. With short intervals now XIII is opened for a moment to admit the gas, dried in q, which then condenses in r, as is evident from the manometer m falling back every time. Not before this falling back ceases, thus indicating r to be wholly filled with the liquid, XIII is shut definitively; then through XI and XV we let boil away some Methylchloride to drive out the more volatile impurities, the less volatile impurities remaining in p

For the Ethylene, (obtained at the Leiden Laboratory itself from alcohol and sulfuric acid, and kept in common iron cylinders under a pressure of 30—45 atm) the process is wholly the same.

As storing cylinders for the Ethylene I used the two strong copper cylinders r' and r'', each provided with a cock. Having two cylinders is useful, first because in this way the quantity of Ethylene stored up is, as is necessary, greater than that of Methylchloride; secondly this arrangement enables us to reach with the Ethylene higher pressures in the experimenting tube, than would be the case in using one greater reservoir; for we first

admit as much as possible of the gas into the experimenting tube, and open r'' not before r' has been shut.

Easily and quickly so much Ethylene may be distilled from the large storing-cylinders into these reservoirs by cooling in alcohol and solid carbonic acid, that pressures of over 100 atm. are reached in returning to the temperature of the room.

6. *Experiments on mixtures of Methylchloride and Ethylene.* By means of the apparatus described above the changes were measured of the capillary ascension with variation of the pressure (the parameter, giving the places of the phases on the connode curve), the temperature remaining constant. The pressure was read from an air-manometer (M. fig. I). In order to obtain the capillary ascension I measured the vertical distance h between the lowest point of the meniscus in the capillary tube, and the lowest point of the meniscus in the annular space, left between the capillary tube and the observation tube.

The real ascension, — i. e. the ascension which the liquid would show, if the capillary tube were placed amidst an infinite horizontal niveau — is obtained, as shown by VERSCHAFFELT, by adding to the measured height the correction

$$h' = h \frac{2d}{\frac{(r_3 - r_2)^2}{r_1} - 2d} + \frac{r_1}{3}$$

in which

h = the ascension as measured
d = the height of the annular meniscus
r_1 = the inner —
r_2 = the outer radius of the capillary tube
r_3 = the inner radius of the observation tube.

The thus obtained real ascensions $H = h + h'$ were then multiplied by $10r_1$, and so I obtained the real ascensions H_1 which would have been measured in a capillary tube with a radius of 0.1 mM. In order to obtain r_1 I used the value of the surface-energy of Methylchloride, which has been measured very exactly by VERSCHAFFELT [1]), who found the real ascension in a capillary tube with a radius = 0.1 mM. to be:

$$H_1 = 42.09 - 0.265\, t.$$

As an example may serve the calibration of the tube IV. In order to estimate the correction h' I used the results of a miscroscopic measurement of r_1 at both ends of the tube

$r_1 = 0.104$ and 0.107 mM.: mean value = 0.106 mM.

r_2 was measured by means of a micrometer

$r_2 = 0.525$ and 0.555 mM.: mean value = 0.540 mM.

By measuring with a cathetometer and by weighing a mercury-column I found

$$r_3 = 3.04 \text{ mM.}$$

Measuring the ascensions h and the height of the annular meniscus d at distances a mM. from the top of the tube, I obtained the following values:

[1]) Not yet published.

t	a	h	d	H	r_1
12°	65	34.84	1.31	36.53	0.1065
»	75	35.00	.30	.69	.1061
»	85	.16	.33	.85	.1056
»	95	.38	.34	37.07	.1050
»	105	.63	.31	.29	.1044
»	115	.78	.32	.47	.1039

I repeated the measurements with a renewed quantity of the liquid, and obtained agreeing results.

In order to obtain the mixtures, the ascension of which has to be measured, we may proceed in two different ways:

1°. Taking a quantity of Methylchloride, we may add repeatedly a small quantity of Ethylene, and so obtain successively several mixtures, each of which contains more Ethylene than the former. Thus at last the phenomena of the plaitpoint will be observed.

As at the temperature of my experiments (10° and 23°) the plait occupies nearly the whole breadth of the ψ-surface, and accordingly the plaitpoint is reached only when a very great quantity of Ethylene is dissolved, it is necessary to begin every time with different quantities of Methylchloride, in order to study different parts of the *Ascension-Pressure-Curve.*

So f. i. the volume of the liquid phase increased in the neighbourhood of the plaitpoint at both temperatures to about 30 or 40 times the original volume, which compelled me, on account of the dimensions of my apparatus, to begin with so small a quantity of Methylchloride, that I was not able to bring the meniscus to the suitable place in the capillary tube, (the quantity

of the liquid being too small), before the pressure had reached ± 30 atmosph. Besides on these occasions however I repeatedly renewed the mixtures, in beginning with a new quantity of Methylchloride, in order to rid myself of possible accidental impurities.

2°. The second way to obtain mixtures of different composition, is to begin with a mixture containing more Ethylene. In repeatedly letting boil off some Ethylene, I successively obtained different mixtures, each of which contained less Ethylene than the former. But also when proceeding in this way, it is necessary to begin with different quantities of Methylchloride, in order to study different parts of the curve.

Both methods I applied in my experiments, and in doing so I obtained well agreeing values.

This was especially the case in my second experimenting series (23°), where particularly the second method of preparing the mixtures, the method of decreasing pressures, led comparatively quickly to a constant result, every time however with the aid of the stirring apparatus. Usually I obtained already constant values of the ascension, after having twice brought the liquid into *C* with the aid of the compound-pump *V* (fig. I), and having stirred it there together with the gas.

With increasing pressures on the contrary, often a 10 times repeated stirring was necessary, before the ascension became constant. Very likely the chief reason of this is, that the small quantity of the liquid that remains in the capillary tube is renewed very slowly and so reaches the thermodynamical equilibrium, ap-

pertaining to the given pressure, only by repeatedly moving the meniscus up and down; with the method of decreasing pressures on the contrary, this small thread of liquid is immediately broken and driven out of the capillary tube by the Ethylene boiling away.

7. *Changes of the capillary ascension with variations of pressure as far as the plaitpoint.* A first series of experiments was made at the temperature of the water from the supply, about 10°.4 C, only a little over the critical temperature of Ethylene (9°). At slightly differing temperatures, I repeatedly observed the decrease of the ascension with increasing pressures as far as the plaitpoint. In the immediate neighbourhood of the plaitpoint however it appeared nearly impossible to obtain constant values, on account of the great disturbances caused there by gravitation and by changes of temperature, even when nearly imperceptible. So f. i. I sometimes noticed a sudden change of the ascension, without any perceptible cause, and sometimes the ascension even turned negative. Yet even then the meniscus remained sensibly concave, thus incontestably proving this phenomenon to be caused by the liquid not being homogeneous within and without the capillary tube. The plaitpoint-pressure at this temperature I derived from the plaitpoint-pressure at 11°.6 — which I found to be 56.07 ± 0.10 atm. — by means of a correction, obtained graphically by using the plaitpoint-pressure (50.15 ± 0.10 atm.) of 23° C., observed in my second series of experiments.

In Table I are given the results of the measurements made at 10°.4 C.

A second series of experiments, the results of which are given in Table II, was made at the temperature of 23°, kept constant by the apparatus described above.

In consequence of the greater distance from the critical temperature of Ethylene and of the temperature being much more constant, I succeeded here much better in obtainiug constant and well agreeing values, as is evident from the graphical representation in fig. VI. There the curve *A* gives the the ascensions and the pressures of pure Methylchloride at different temperatures. The two series of observations concerning the mixtures of Methylchloride and Ethylene at 10°.4 and at 23° are represented by the curves *B* and *C*.

Table I.

Ascension-Pressure-curve at 10°.4 C.

$t.°$ C	$P.$ atm.	H_1 mM.
10°.4	3·60	39.33
2	15.30	30.13
4	19.54	26.96
6	23.61	23.50
3	29.50	19.64
2	32.17	17.74
3	37.93	14.24
2	39.65	13.49
4	44.05	10.55
3	46.28	8.67
4	49·10	6.55
2	52.04	3.63
4	55.20	Plaitpoint (derived from that at 11°.6.).

Table II.

Ascension-Pressure-curve at 23°.0 C.

$t°.$ C.	$P.$ atm	H_1 mM.
23.00	5.25	36.00
14	20.62	25.16
08	26.45	23.20
15	30.64	18.50
05	35.20	15.53
15	40.71	12.40
07	41.56	11.79
00	43.26	10.92
02	45.85	9.71
07	50.74	7.39
07	52.48	6.20
00	54.11	4.92
00	59.15 ± 0.09	Plaitpoint.

Fig. I.

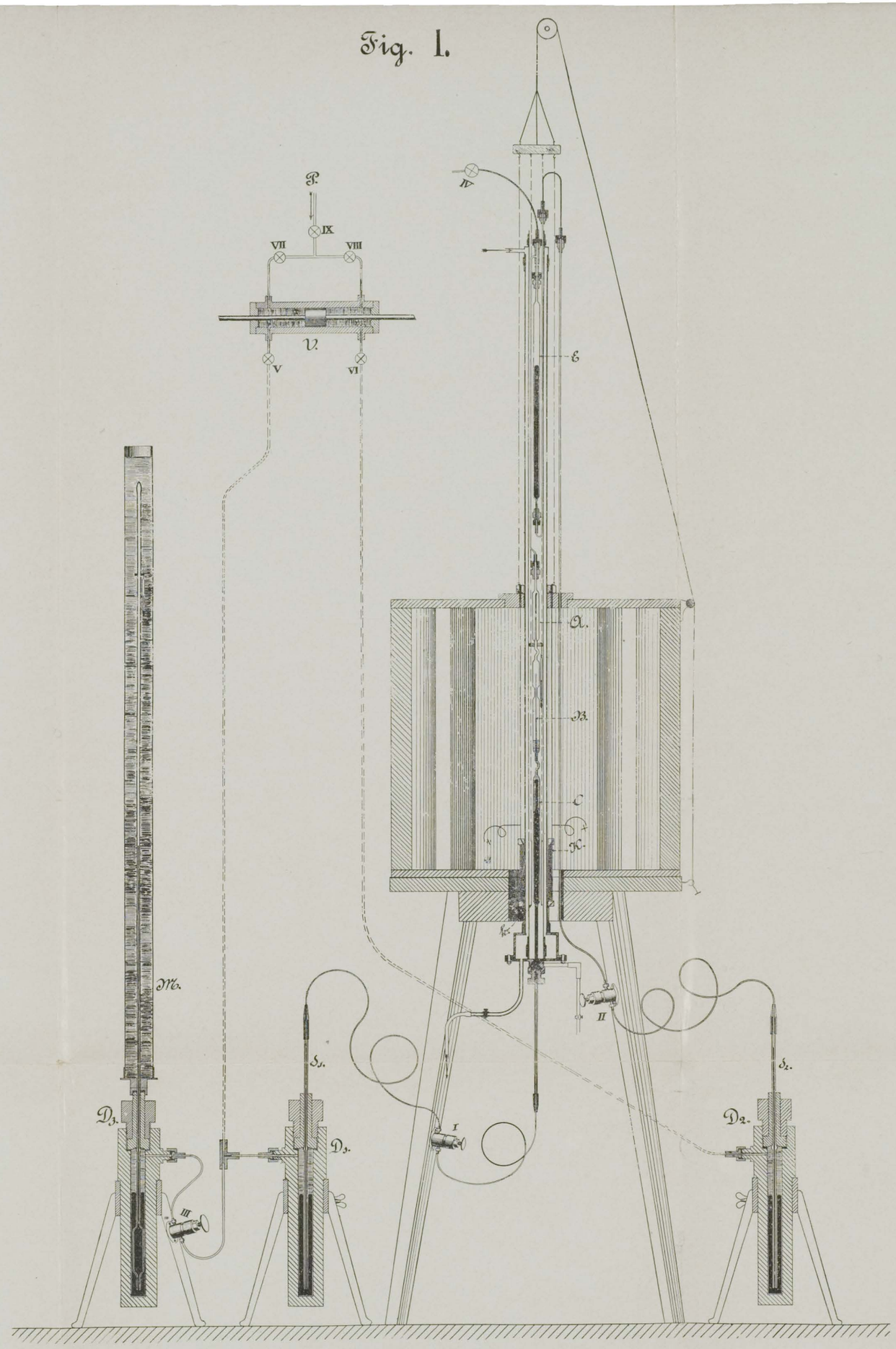
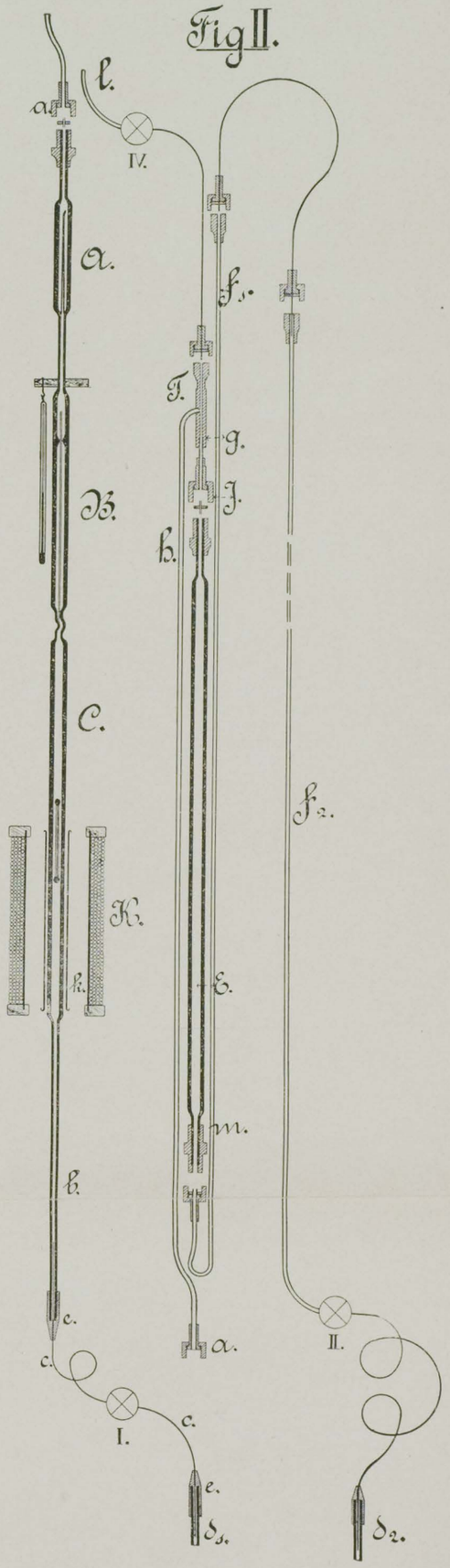


Fig II.



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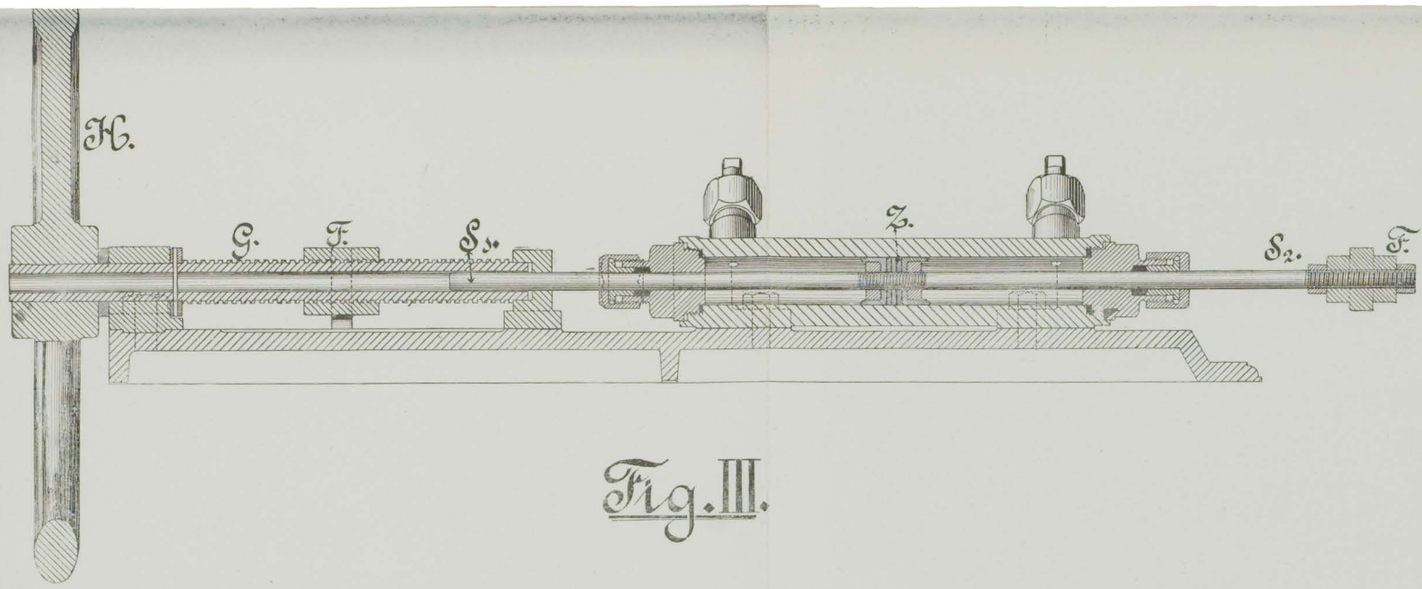
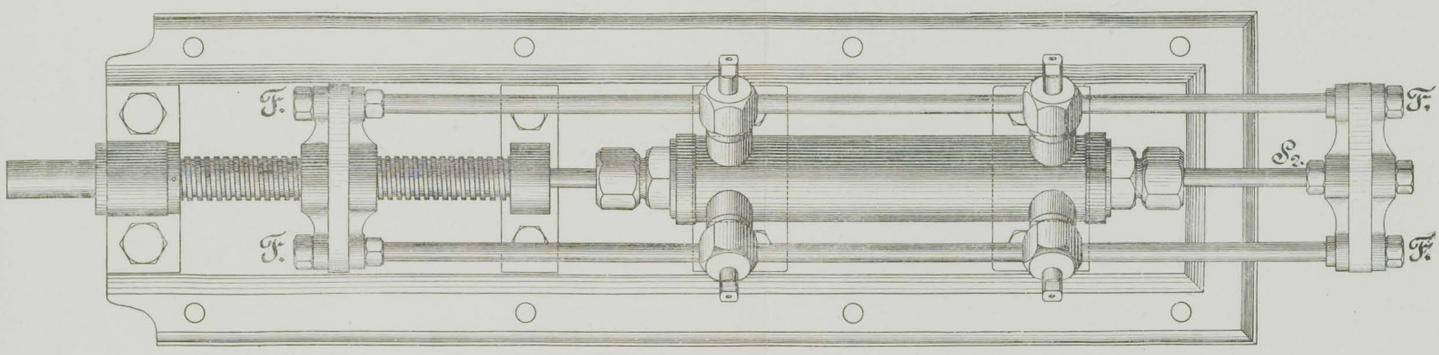


Fig. III.



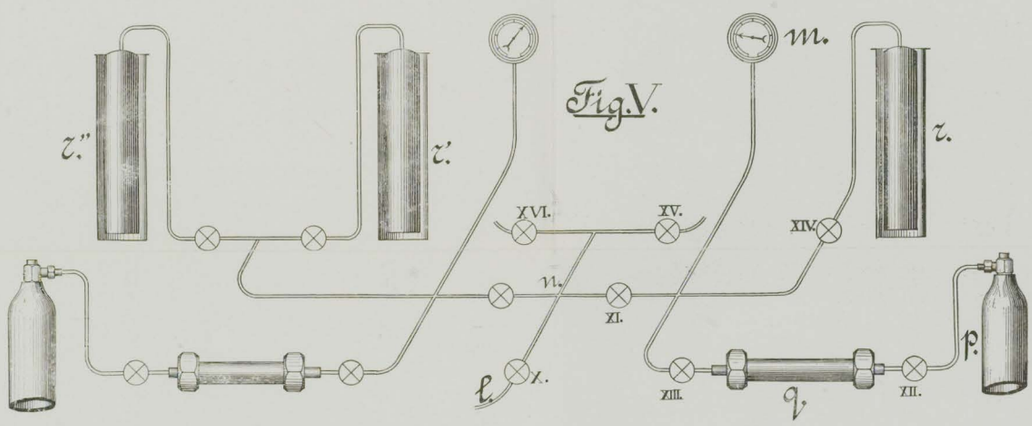


Fig. V.

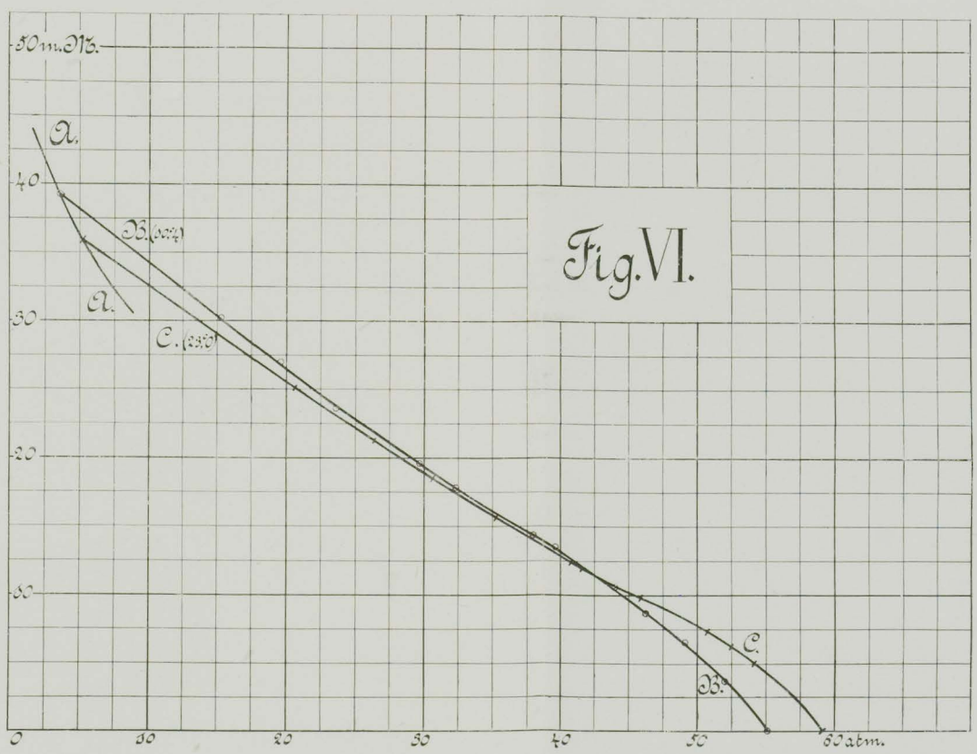


Fig. VI.