size of the molecule of the normal substance has influence on the course, has also lost its direct importance. For mixtures of ethane with an alcohol the separation between the two types lies between methyl- and ethylalcohol; the question whether this separation takes place between two higher terms of the alcohol series, if we take instead of ethane a higher term of the series of carbonhydrogene compounds, which seemed very important before is now no longer of primary interest [1]). It seems to me that I have to return in many respects to my original meaning, namely that we have to inquire after the circumstance which causes the spinodal curve to show a protuberance towards the side of the small volumes. In mixtures of a normal substance with an associating one this cause can perhaps be found in the circumstance that the quantity $\left(\frac{\partial p}{\partial x}\right)_v$ can obtain abnormous high values for such a mixture. As the equation:

$$-\frac{\partial p}{\partial v}\frac{\partial^2\psi}{\partial x^2}=\left(\frac{\partial p}{\partial x}\right)^2$$

applies to the spinodal curve, the value of $-\frac{\partial p}{\partial v}$ may also be abnormously high in this case. If this is really the case an explanation for the protuberance is given which is certainly satisfactory. Yet a great distance exists between this observation and an adequate calculation.

In any case these experiments of KUENEN, to which I hope that he will add many others, are an important contribution to our knowledge of the critical phenomena of not miscible substances.

Physics. — "*The influence of variation of the constant current on the pitch of the singing arc.*" By J. K. A. WERTHEIM SALOMONSON. (Communicated by Prof. P. ZEEMAN).

In the course of some experiments on the physiological action of alternating currents of very high frequency, I tried the currents generated by means of DUDDELL's singing arc. A constant current arc between solid carbons shunted by a self-inductive resistance and a condenser emits a note, the pitch of which corresponds with the frequency of the alternate current generated in the condenser-circuit.

[1]) An experiment in order to investigate whether for propane the limit lies between ethyl- and propylalcohol was already in preparation for a long time in the laboratory of Amsterdam. But other labour which could not be delayed prevented each time those who would undertake the investigation.

DUDDELL believed that the frequency was determined by the self-induction and the capacity according the well-known formula: $p = 2\pi\sqrt{cL}$.

PAUL JANET thought the same and proposed, as DUDDELL had already done before, to use the singing arc for measuring small coefficients of self-induction.

In the way proposed by JANET, this seems to be impossible as the frequency depends not only on the self-induction and the capacity but i. a. also on the strength of the constant current.

I have investigated the variation of the frequency caused by varying the constant current, the results being stated in this paper.

The experiments were carried out after PEUKERT's method. The PD at the solid carbons was measured by a Weston-instrument, that showed the Volts of the constant current only, and at the same time by a hot-wire Voltmeter. Lastly the current in the condenser-circuit was measured by means of a hot-wire amperemeter. The three readings being E_1, E_2 and I_2, the frequency may be calculated by

$$p = \frac{I_2}{2\pi c\sqrt{E_2^2 - E_1^2}},$$

c being the capacity of the condenser in farads.

The necessary correction of the instruments was known and has already been applied in the tables. The arc-lamp used was a small shunt-regulator by KÖRTING & MATTHIESEN.

Series 1. Capacity 2,68 mF. Selfinduction: bronze wire spiral of 80 windings; air isolation; diameter 25 centimeter, height 50 centimeter.

The table contains in the

1st column:	I_1	the constant current through the arc.
2nd "	E_1	the constant current PD of the carbons.
3rd "	E_2	the hot-wire voltmeter reading.
4th "	E_a	the value of $\sqrt{E_2^2 - E_1^2}$ being the superposed alternating volts.
5th "	I_2	the alternating current strength.
6th "	p	the number of complete alternations p. s. calculated by PEUKERT's formula.

TABLE I.

I_1	E_1	E_2	E_a	I_2	$p.$
1.9	37.0	44.0	23 7	1.8	4520
2.2	37.0	46.0	27.4	2 4	5230
2.6	37.5	43 0	21 1	2.1	5960
2.8	37.5	44.0	23.0	2.4	6450
3.2	38.0	42.7	19 6	2.5	8000
3 7	38.0	41.0	15.5	2 7	10390
4.1	38.0	40.0	12 8	3.0	13980

Series 2. The same as in Series I. Capacity reduced to 1.68 mF.

TABLE II.

I_1	E_1	E_2	E_a	I_2	$p.$
1.7	38	46	26	1.7	6200
2.4	39	46	24.5	2.1	8130
2.8	39	44	20.4	2.1	9820
3	38	42.7	19.6	2.3	11200
3.5	38.5	42	16.75	2.4	13590
3.7	38	42	18.3	2 7	13980

Series 3. Capacity 1 mF. Selfinduction: coil of 160 windings in 4 layers; wire 2 millimeters. Length of coil 8 centimeters, external diameter 3.5 centimeter.

TABLE III.

I_1	E_1	E_2	E_a	I_2	$p.$
1.9	38	47.7	28.7	2.4	14950
2.3	38	47	26	2.6	17240
2.6	38	45	24 5	2.9	18820
2.9	38	43	20.1	2.8	22200
3.3	37	42	19.8	3.3	26600
3.6	37	42	19.8	3.5	28160
4.1	38	41	15.4	3 4	35100

Series 4. The same as Series III. Capacity reduced to 0.5 mF.

TABLE IV.

I_1	E_1	E_2	E_a	I_2	p.
1.9	35	47	31.3	2 51	25200
2.4	36	42	21.6	2 51	36800
2 7	35	40	19 4	2 7	44300
3.1	35	39	17.2	3	55550
3.4	35	37	12	3.2	84700
3.7	35	36.5	10.36	3.3	97700
3.9	35	36 5	10.36	3.4	100500

Series 5. Capacity 1 mF. Selfinduction: coil of 40 windings in 2 layers; wire $3^1/_2$ mm. Length of coil 8 centimeter, external diameter 3.5 centimeter.

TABLE V.

I_1	E_1	E_2	E_a	I_2	p.
1 9	38	50.4	33 2	4.68	22400
2 2	38	50.4	33 2	5.16	24700
2.6	38	50.4	33.2	5 55	26700
2 9	38	46	26 0	5.20	31800
3.2	37.6	46	26.5	6 15	37000
3 6	37	44	23.8	6.15	41200
3 7	38	43.2	22.8	6 24	43600
4 2	38	41	15.4	5.70	59200

Series 6. The same conditions as in Series 5. The capacity reduced to 0.3 mF.

TABLE VI.

I_1	E_1	E_2	E_a	I_2	p.
2 1	35	50	35.7	4 1	61300
2.4	36	47.5	31	4.2	71900
2.9	35	42	23.2	4	91600
3 6	36	40.2	17 9	4.4	130000
4.2	35	36.3	9.75	3.6	196000

Duddell attained frequencies of 500—10000 complete periods p. s. Simon increased the number of alternations so much, that the note emitted by the arc ceased to be audible. He speaks of a limit of 30000—40000 vibrations. From my tables will be seen that I have attained much higher frequencies, so high that I first distrusted them. But as yet I have not been able to find any inaccuracy either in the principle of the method or in its application. So I must think that my numbers are exact, the more so as they seem to be confirmed by a physiological estimate. With small frequencies, say up to 10000, the pitch of the note may be easily estimated by the ear when we produce two notes in rapid succession. In Series 1 I found that increasing the current from 1.9 to 2.2 ampere caused the pitch to rise about a "second". By increasing from 2.2 ampere to 3.2 ampere the successive notes sounded as with a quint-interval. The later calculation of the frequencies from the galvanometer readings agreed fairly well with the estimated increase of pitch.

The limit of audibility as calculated from the readings agreed equally with the limit as determined by the aid of a recently graduated Galton-whistle by Prof. Edelmann, the graduation-table being verified on different points by myself. I found as a limit for the audibility about 43500 d. v. p. s. My arc-lamp ceased to emit an audible note when the frequency of 42000 was reached. In the 6th series no sound was heard at all. In the series 1, 2 and 3 the sound was heard throughout. In the series 4 I heard the note distinctly at 2.4 ampere; at 2,7 ampere I did not always hear the sound; only every now and then I got the impression of a very faint and high whistling sound. At 3.1 ampere I did not hear the sound. In the 5th Series the sound was always present at 3.6 ampere and sometimes at 3.7 ampere.

As these results agree, I think that the method is a correct one, and that the higher numbers may also be relied upon.

The sound of the singing arc may prove perhaps valuable in physiological researches on sound.

The highest frequency with my apparatus was attained with a primary constant current of 4.2 ampere, $E_1 = 36$ Volt, $E_2 = 37.3$ Volt, $I_2 = 0.49$ ampere, $C = 0.03$ m.F., E_a being 9.7 Volt and $p =$ **268000**. Of course much higher frequencies may probably be attained. But the resistance of my hot-wire amperemeter was rather high, and I believe that therein lies an obstacle for my surpassing this limit.

How are we to interpret the increase of the frequency caused by an increase of the constant current? There is some analogy with the rise in pitch of electromagnetically driven tuningforks when the intensity of the currents is increased; and also with the rise of the pitch of harmoniumreeds when the air-pressure is increased: Yet there is already some difference in the origin of these last two phenomena, so as to forbid anything more than considering the analogy. The only allowed consequence is, that the electrical system consisting of a capacity and a selfinduction does in this special case not vibrate in its proper period and that this proper period might only be expected to be brought about by a hypothetic infinitely small constant current through the arc.

Increasing the P. D. at the carbons seems to lower the pitch and at the same time to increase the intensity of the sound; if the P.D. rises too much the whistling ceases all at once. As I worked with a constant E. M. F. of 110 Volts from an accumulator-battery, the primary current strength was regulated by inserting resistance or withdrawing it from the circuit. When without changing the resistance, the P. D. at the carbons rises, the current falls off and so causes the frequency to diminish at the same time. Yet by keeping the current constant, by lengthening the arc and withdrawing resistance at the same time an unmistakable lengthening of the period may be observed.

From the Tables I—VI curves have been plotted connecting the frequency with the current-strength.

It is not impossible, that a simple relation might express this connection. Yet an experimental formula as

$$p = a + bI + cI^2$$

is only possible when b is negative; as in this case there is a minimum for $I = \frac{b}{2c}$ this formula does not seem to be very plausible.

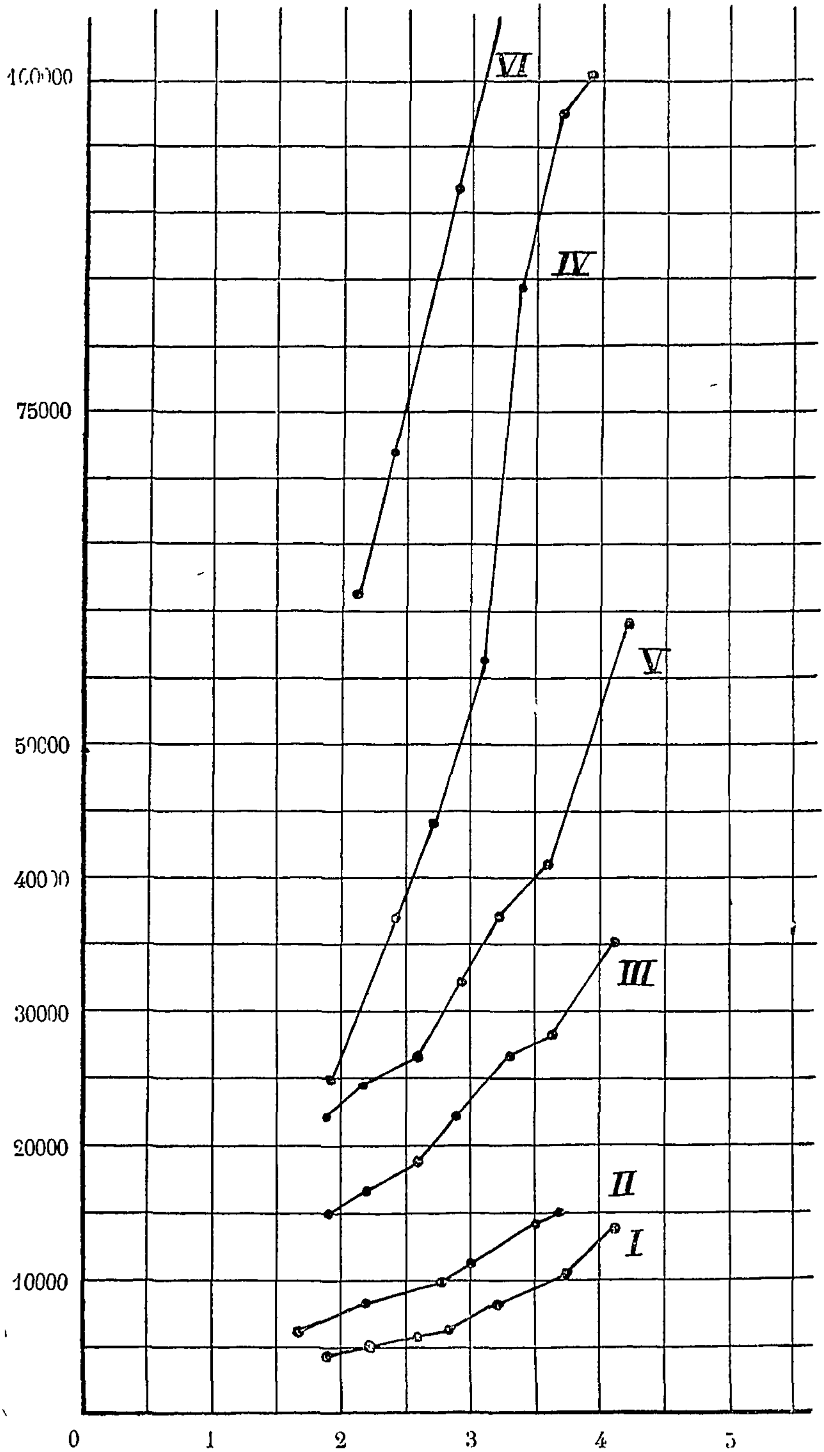
I have also tried a quadratic expression connecting the steadying resistance with the frequency, but this did not give satisfaction.

At last I found as the most simple formula and agreeing best with the observed results:

$$\log p = a + bI,$$

in which a and b are constants, p the frequency and I the constant current intensity.

I found for series 1:


100000
75000
50000
40000
30000
20000
10000
0
1
2
3
4
5
VI
IV
V
III
II
I

$$log\ p = 3.23522 + 0.2165\ I.$$

I	$log\ p$ (calc.)	$log\ p$ (obs.)	ρ	p (calc.)	p (obs.)
1.9	3.64757	3 65514	+ 0.00857	4432	4520
2.2	3.71152	3.71850	+ 0.00698	5147	5230
2.6	3.79812	3.77525	— 0.02287	6282	5960
2.8	3.84142	3.80956	— 0.03186	6941	6450
3.2	3.92802	3.90309	— 0.02493	8473	8000
3.7	4.03627	4.01662	— 0.01965	10871	10390
4.1	4.12287	4.14364	+ 0.02077	13270	13920

The mean error of $log\ p$ being: $\sqrt{\frac{1}{6}\Sigma(\rho)^2} = 0{,}02272$ the error-factor of p is 1.053 and the mean error of p is 5.3 %.

Considering that 3 galvanometer readings are necessary which individually ought to have errors of much less than 0.5 %, but which are to be taken all at the same time and therefore are more inaccurate, a mean error of 5.3 % in the result, representing an interval of less than a tone may not be called extravagant.

For series 2. I find: $log\ p = 3.47786 + 0.18453\ I.$

I	$log\ p$ (calc.)	$log\ p$ (obs.)	ρ	p (calc.)	p (obs.)
1.7	3.79156	3.79239	+ 0.00083	6189	6200
2.4	3.92073	3.91009	— 0.01064	8332	8130
2.8	3.99454	3.99211	— 0.00243	9875	9820
3 0	4.03145	4.04922	+ 0.01777	10751	11200
3.5	4.12371	4.13322	+ 0.00951	13296	13590
3.7	4.16062	4.14551	— 0.01511	14475	13980

$$\rho\ m = \sqrt{\frac{1}{5}\Sigma(\rho)^2} = 0.01228$$

the mean error of one observation being 2.867 %.

Series 3. $log\ p = 3.84563 + 0.17062\ I.$

I	$log\ p$ (calc.)	$log\ p$ (obs.)	ρ	p (calc.)	p (obs.)
1.9	4.16981	4.17464	0.00483	14785	14950
2.3	4.23806	4.23654	0.00152	17300	17240
2.6	4.28927	4.27462	0.01465	19466	18820
2.9	4.34043	4.34635	0.00592	21900	22200
3.3	4.40868	4.42488	0.01620	25626	26600
3.6	4.45986	4.44963	0.01023	28831	28160
4.1	4.54517	4.54531	0.00014	35089	35100

$$\varrho\ m = \sqrt{\frac{1}{6} \Sigma (\varrho)^2} = 0.01035$$

mean error of one observation 2.412 %.

Series 4. $log\ p = 3.80102 + 0.31641\ I.$

I	$log\ p$ (calc.)	$log\ p$ (obs.)	ρ	p (calc.)	p (obs.)
1.9	4.40220	4.40140	− 0.00080	25247	25200
2.4	4.56280	4.56585	+ 0.00305	36542	36800
2.7	4.65532	4.64640	− 0.00892	45219	44300
3.1	4.78189	4.74468	− 0.03721	60519	55550
3.4	4.87681	4.92788	+ 0.05107	75303	84700
3.7	4.97174	4.98989	+ 0.01815	93700	97700
3.9	5.03502	5.00217	− 0.03285	108400	100500

$$\varrho\ m = \sqrt{\frac{1}{6} \Sigma (\varrho)^2} = 0.02994$$

mean error of one observation 7.14 %.

Series 5. $log\ p = 3.98960 + 0.17902\ I.$

I	$log\ p$ (calc.)	$log\ p$ (obs.)	ρ	p (calc.)	p (obs.)
1.9	4 32974	4.35025	+ 0.02051	21367	22400
2.2	4.38344	4.39270	+ 0.00926	24179	24700
2.6	4 45505	4 42651	− 0.02854	28513	26700
2 9	4 50876	4.50243	− 0.00633	32267	31800
3.2	4.56246	4.56820	+ 0.00574	36514	37000
3.6	4.63407	4.61490	− 0.01917	43060	41200
3.7	4.65197	4.63949	− 0.01248	44871	43600
4 2	4.74148	4.77232	+ 0 03084	55141	59200

$$\rho\, m = \sqrt{\frac{1}{7} \Sigma (\rho)^2} = 0.02024$$

mean error of one observation 4.77 %.

Series 6. $log\ p = 4.31949 + 0.22466\ I.$

I	$log\ p$ (calc.)	$log\ p$ (obs.)	ρ	p (calc.)	p (obs.)
2.1	4.79128	4.78746	− 0.00382	61841	61300
2.4	4.85867	4.85673	− 0 00194	72222	71900
2.9	4.97100	4.96190	− 0.00910	93540	91600
3.6	5 12827	5 11394	− 0.01433	134360	130000
4.2	5 26306	5.29226	+ 0.02920	183257	196000

$$\rho\, m = \sqrt{\frac{1}{4} \Sigma (\rho)^2} = 0.01702$$

mean error of one observation 4.00 %.

The empirical formula represents fairly well the observed results in the range of the experiment. But it does not give more than that, I do not think that it may be used for extrapolating. This will be directly seen, when we extrapolate for the intensity = 0. We calculate for the frequency at the intensity = 0 in the 4th series: 6324 d. v. and in the 3rd series: 7009 d. v. Theoretically the frequency in series 4 should be exactly $\sqrt{2}$ times higher than in series 3.

A more exact method may perhaps give numbers from which a better formula might be deduced, and which at the same time might give us some insight in the phenomenon.

I have tried to get more exact numbers by means of the KUNDT dust-figures but I did not succeed, though others might. Yet the oscillatory discharge of a Leyden jar through an inductive resistance easily gave regular dust-figures. The reason why the KUNDT-method proved refractory with the singing arc, is not easy to be understood: I can only suppose that the intensity of the sound is not large enough.

Physics. — Dr. J. E. VERSCHAFFELT. "*Contributions to the knowledge of* VAN DER WAALS' *ψ-surface. VII. The equation of state and the ψ-surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components*". Communication n°. 81 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES. [1])

(Communicated in the meeting of June 28, 1902).

Introduction.

In Communication n°. 65 from the Physical Laboratory at Leiden [2]) I have given the first results of a treatment of my measurements on mixtures of carbon dioxide and hydrogen [3]) by the method which KAMERLINGH ONNES [4]) alone and with REINGANUM [5]) used for the measurements of KUENEN on mixtures of carbon dioxide and methyl chloride [6]). They confirm KAMERLINGH ONNES' opinion that the isothermals of mixtures of normal substances may be derived, by means of the law of corresponding states, from the general empirical reduced equation of statefor which he has given in communications nrs. 71 [7]) and 74 [8]) a development in series indicated in communication 59*a*. In this empirical reduced equation of state

$$\mathfrak{p} = \frac{\mathfrak{A}}{\lambda \mathfrak{v}} + \frac{\mathfrak{B}}{\lambda^2 \mathfrak{v}^2} + \dots ,$$

[1]) The translation of the first and second part of this article are treated as a whole, hence some minor changes in text will be found.

[2]) Arch. Néerl., (2), 5, 644, 1900; Comm. phys. lab. Leiden, n°. 65.

[3]) Thesis for the doctorate, Leiden, 1899.

[4]) Proc. Royal Acad., 29 Sept. 1900, p. 275; Comm. 59*a*.

[5]) Ibid. p. 289; Comm., n°. 59*b*.

[6]) Thesis for the doctorate, Leiden, 1892.

[7]) Proc. Royal Acad., June 1901; Comm., n°. 71.

[8]) Arch. Néerl., (2), 6, 874, 1901; Comm., n°. 74.