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Physiology. — *"Specific smell intensity and the electrical phenomenon of cloudlike condensed water vapours in chemical series."*

By Prof. Dr. H. ZWAARDEMAKER.

(Communicated in the meeting of May 27, 1916).

In the meeting of the 25th of March 1916 we set forth that all true odorous substances have the property of imparting an excess of electro-positive charge to the cloudlike condensed water-vapour, generated by spraying an aqueous solution under an overpressure of two atmospheres. The attending negative charge is in the air. Contrary to this, pure water [1]) and aqueous solutions of salts, inodorous substances, sugars, ureum etc. sprayed in the same way, give a cloud containing both charges, which persist in the case of salts.

A screen, arranged to block the way of the spray, intercepts a very strong charge in the case of the odorous substances, but is not electrified in the case of the above-mentioned inodorous liquids, unless under special circumstances that give rise also to waterfall-electricity. Not before the screen approaches the insulated sprayer very closely, or before the surrounding air has been purposely ionized (e.g. through an electric field), does a charge appear; in the latter case, also on the distant screen. This charge is identical with the charge arising spontaneously if the water in the earth-connected sprayer had been impregnated with even the merest trace of an odorous substance.

This odoroscopic phenomenon I have correlated with:

1) Pure water, diffused through a sprayer, going obliquely upwards, gives a positively charged spray, as has been shown in experiments by P. LENARD in 1898. The amount of electricity was per gram of sprayed water 7.10^{-10} coulomb. (P. LENARD, ü. Wasserfallelektricität, Ann. d. Physik (4). Bd. 47, 1915, p. 479) EVE's water-sprayer gave distinct electricity of either sign (negative to excess) only to a purposely charged electrometer. (A. S. EVE, Ionization by spraying, Phil. Mag. (6) Vol. 14 p. 382 1907). J. C. POMEROY again succeeded in catching up the positive drops while the negative electricity remained in the air. (Phys Rev. Vol. 27 p. 492, 1908). It attracts notice that he also placed the sprayer above the reservoir. In all these cases, however, very small, just noticeable quantities of electricity were dealt with (A. BECKER, Jahrb. d. Radioaktiv. u Elektronik, Bd IX, 1912, p. 79). The electroscope (EXNER-type), used in my experiments, was not sensitive at all. The aluminium-leaves were of the usual width, but rather short. They deflected at a charge of 220 Volts 10 scale-divisions of a milimeter scale. The charges produced by the odorous clouds induced much larger, even maximal deflections within some moments. They were of the order of 100.10^{-10} coulomb per gram of sprayed solution, with an earthed sprayer.

1. molecular weight,
2. volatility,
3. lowering of the surface-tension of the solvent, the same factors being, to a certain degree, essential to render a substance odorous. I particularly wish to lay stress on the second and the third factor by observing that odorous substances lower the surface-tension of water, that they are volatile, and that, on the contrary, not all volatile substances, lowering the surface-tension, must of necessity be odorous substances. If my view is correct we may rationally expect a relationship to exist between the smell intensity of a substance and the intensity of the electrical phenomenon. This relationship will appear in its simplest form with homologous series.

In the literature mention has been made of two homologous series that have been carefully studied as to smell intensity. They are the aliphatic alcohols to the fifth term and the fatty acids to the tenth. PASSY [1]) determined the smallest quantity of matter, diffused in a litre of air, capable of arousing olfactory sensation. When we divide this smallest quantity, expressed in grams by the molecular weight, the reciprocal of the number is an index for the specific smell intensity. This leads to the following results.

By plotting the molecular weights along the axis of the abscissae and the molecular smell intensities along the axis of the ordinates we get curves of a regular shape.

Likewise graphs may be made of the electrifying power of the clouds.

When we place a circular tin disc 50 cm. in diameter, in the drift of an odour-solution from an earthed sprayer, at only 1 or 2 mm.

TABLE I.
Aliphatic alcohols.

Terms	Min. perc. gr. per Litre PASSY	Mol. weight	Specif. smell intens.	Log. mol. smell intens. —4
Methylalcohol	1000.10^{-6}	32	$0.032.10^{6}$	0.51
Ethyl "	250.10^{-6}	46	$0.18\ .10^{6}$	1.26
Propyl "	10 à 5.10^{-6}	60	$6\ .10^{6}$	2.78
Butyl "	1.10^{-6}	74	$74\ .10^{6}$	3.87
Isoamyl "	$0,1.10^{-6}$	88	$880\ .10^{6}$	4.94

[1]) JACQUES PASSY. Comptes rendus 16 Mai 1892 and 1 Mai 1893.
[2]) H. ZWAARDEMAKER in TIGERSTEDT's Hdb. der physiol. Methodik. Bd. III, S. 57.

TABLE II.
Fatty acids

Terms	Min. perc. gr. per Litre Passy	Mol. weight	Specific smell int.	Log. mol. smell int. - 6
Formic acid	25.10^{-6}	46	$1.8.10^{6}$	0.26
Acetic acid	5.10^{-6}	60	$12.0.10^{6}$	1.08
Propionic acid	$0.05.10^{-6}$	74	1480.10^{6}	3.17
Butyric acid	$0.001.10^{\ 6}$	88	88000.10^{6}	4.94
Valerianic acid	$0.01.10^{-6}$	102	10200.10^{6}	4.01
Caproic acid	$0.04.10^{-6}$	116	2900.10^{6}	3.46
Oenanth acid	$0.3.10^{\ 6}$	130	430.10^{6}	2.63
Caprylic acid	$0.05.10^{-6}$	144	2880.10^{6}	3.46

distance of the vertical nozzle, no charge will be generated [1]). An equal number of positive and negative nuclei splash against the disc and the algebraic sum of the charges is 0. On increasing the distance between the disc and the nozzle, while remaining well-insulated, the positive charge soon manifests itself, then gradually increases, until it reaches a maximum at a certain optimum. Later on it diminishes again, till it is reduced to zero, at a distance sharply defined for every substance. At this juncture we may say that all positive drops, produced in excess by the cloud, are present in or drop down from a cone whose vertex is the nozzle of the spraying tube and whose base is constituted by the part of the disc moistened by the cloud. The original negative nuclei, generated likewise by the cloud, are lost.

As soon as the spraying has become fairly continuous we may assume that on this side of the disc, placed at the critical distance, the number of positive drops that descend is equal to that of negative ones that disperse in the surrounding air, while moreover an equal number of either sign dash against the base of the cone. At some spots an excess of positive droplets is present in the cone e.g. on a small disc, when placed at a shorter distance. Besides this, continually some fall down. If we were sure to catch up all the falling droplets and to determine their aggregate weight, we should possess a simple means to estimate the charge of an odorous cloud. J. C. Pomeroy [2], has availed himself of this artifice to detect the faint charge imparted

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1) With an earthed sprayer pure water yields no charge, while with a sprayer insulated by amber it electrifies small discs.

2) J. C. Pomeroy, Phys. Rev. vol. 27, p. 492, 1908.

also by sprayed water to the heavier particles of a cloud [1]). For the present I prefer, for technical reasons, to take roughly, empirically in taking the axis of the cone for index, on the one hand because its length corresponds with the distances to which the large positive and the smaller negative ions are dashed away or rebound, when sent adrift by a constant force, on the other hand because it enables us to realize that the space is large enough to balance, at least on a distant disc, the contrast between positive and negative electricity evoked by the odorous substance.

In carrying out the experiment care was taken to allow sufficient time, for the determination of the faint charge, since it is obvious that, in view of the large size of the disc, its capacity should not be neglected, so that several seconds will elapse before a sufficient amount of electricity has been obtained to be visible on the electroscope.

The results are to the following effect:

TABLE III.

Aliphatic alcohols	Critical distance (cm.)		
	0.3 n.	0.2 n.	0.1 n.
Methylalcohol	46	26	3
Ethylalcohol	103	70	35
Propylalcohol	145	80	72
Butylalcohol	170	100	117
Isoamylalcohol	187	135	130

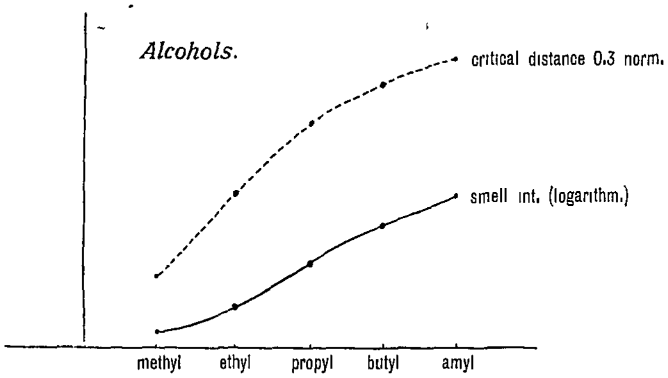

Fig. 1.

1) No manner of charge was given in our experiments by pure water under the experimental conditions, carefully observed, viz. an overpressure of two atmospheres, perfect cleanness of sprayer, glass vessels, air-chamber of 2 m^3. capacity, long metallic pressurecircuit.

A combined graph of Tables I and II may be obtained by plotting the molecular weights against either the logarithms of the specific smell intensities or the critical distances. The curves will then be seen to rise correspondingly and to run roughly parallel.

TABLE IV.

Fatty acids	Critical distance (cm.)						
	1/10 norm. sol.	1/20 n.	1/40 n.	1/80 n.	1/160 n.	1/320 n.	1/640 n.
Formic acid	1.2	no charge					—
Acetic acid	20	0.5					2
Proprionic acid	81	50					20
Butyric acid	125	85					74
Valerianic acid	170	173					78
Capronic acid	—	190	180	177	160	132	106
—	—	—	—	—	—	—	—
Caprylic acid	—	—	—	—	—	—	90

N. B. Below 1/40 n. great care has been taken to keep up the spraying precisely 1/4 min.

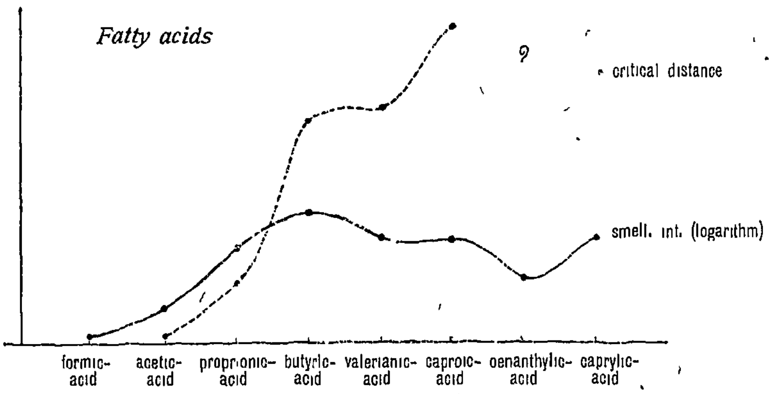

Fig. 2.

A combined graph of Tables II and IV may be obtained by plotting the molecular weights against either the logarithms of the specific smell intensities, or the critical distances The curves thus obtained are not so regular and similar as in the case of alcohols, nevertheless they are of the same type.

Our object in doing this is to compare a physiological with a physical property, each depending on the volatility of the substance and the capacity of lowering the surface tension of water.

Therefore it avails to measure at the same time the surface tension. In the case of pure substances it does not exert a special influence upon the shape of the curve. In the case of water it does. Mr. H. R. KNOOPS was kind enough to investigate this for the fatty acids.

TABLE V.

Number of droplets falling from TRAUBE's Stalagmometer the standard for water being 51.

Fatty acids	$^1/_{20}$ n.	$^1/_{40}$ n.	$^1/_{640}$ n.
Formic ac.	51	51	51
Acetic ac.	57	56	53
Proprionic ac.	58	57	53
Butyric ac	70	68	53
Valerianic ac	88	72	53
Caproic ac.	—	72	54
—	—	—	—
Caprylic ac.	—	—	53

In the series of fatty acids about which we know most, smell intensity and electric power agree in that, while running up in the lower terms, they first increase till they reach a maximum at a certain point, then suddenly weaken in order to fade out in the end. The factor, which, as I think, dominates the olfactory and the electrifying property, viz. that of lowering the surface tension, maintains itself till the series is far advanced, for myristin acid still reduces the surface-tension distinctly (it arrests the camphor-movement and, when added to water to saturation, its number of drops in a given volume is 60, that of water being 51), but it does not evoke the electrical phenomenon, and is at the same time inodorous. It is not improbable that this has something to do with its lack of volatility. I cannot say, however, which of the two properties: the electrical phenomenon or the olfactory capacity goes farther in the homologous series, as caprylic acid was the highest term at my disposal, and this substance still evinces both properties. According to PASSY lauric acid is the terminal smell stimulus in the series.

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Smell intensity and electric power do not reach their maximum at the same term. For the former it occurs with butyric acid, for the latter with caproic acid. A physiological property cannot, indeed, be entirely dependent on merely physical factors. Material volatility e.g. may be a matter of necessity for smell; once afloat odorous molecules are at the mercy of currents of air and diffusion. Further on, in the olfactory fissure adsorption to a moist surface is necessary, but a great number of glands cause the chemical composition of the moist layer, and consequently also the surface qualities to vary from those of water.

Finally the adhesion of the odorous particles to the olfactory hairs is certainly a necessary condition, but the influence they exert is not determined by the degree of adsorption alone. The mere fact that the curves roughly point to such a close relation between the electrifying power and olfactory capacity is remarkable.

A more accurate quantitative measurement of the electric phenomenon may still be obtained by arranging a small disc of just the right size at the critical distance of the sprayer and by allowing the positive drops to beat against it, while the negative ions rebound and disperse. From the time required for a definite deflection, under an overpressure of precisely two atmospheres, or from the deflection brought about by a definite amount of an odour-solution, say 25 c.c., the electrifying power may directly be estimated. An inquiry is now in progress, but of course it will not enable us to point out a closer relation than has already been revealed.

The other series of substances, inodorous yet evoking an electrical charge, has in so far as I was able to ascertain, the property of being soluble in water, of lowering its surface-tension, and moreover of being sublimable. Whether with these substances (antifebrin, antipyrin, caffein, etc.) there is any relationship between the electrical phenomenon and the intensity of physiological action is a question that must be left for further investigation. Many times already experimenters have been looking for a relationship between surface-forces and physiological or toxic effects among chemically allied substances, but their efforts concerned the surface forces acting upon lipoid membranes. In the case of odorous substances in an homologous series we have to do with the action of surface forces upon a capillary layer of water, which no doubt is a much simpler question.