

Citation:

H. Zwaardemaker, The Electrical Phenomenon in Smell-mixtures, in:
KNAW, Proceedings, 19 I, 1917, Amsterdam, 1917, pp. 551-555

Physiology. — "*The Electrical Phenomenon in Smell-mixtures*".

By Prof. Dr. H. ZWAARDEMAKER.

(Communicated in the meeting of September 30, 1916).

In ordinary life it has long been known that there are certain smells that neutralise each other. It is very difficult, however, to mix them experimentally in the right proportion to find the compensation-point i.e. the point at which they cancel each other completely. This is 1. because the constituents mostly volatilise unevenly (directly after the mixing because the solubility is mutually modified; later on through a difference of evaporation); 2. because the migrating odorous molecules generally diffuse with various rapidity; 3. because of the disproportionate adsorption of the smell-mixtures to the sides of phials, beakers etc., used in examining the mixture.

The difficulties to be obviated, are such as to render it next to impossible to find the compensation-point by mixing odorous fluids. In the perfume-industry and in pharmaceutical practice a moderate stability of the resultant odour should, therefore, be valued as a fairly satisfactory result.

The ascertainment of these proportions induced me, in the year 1888, to produce inodorousness by mixing the odorous gases themselves. Well-known, purely chemical odours were then combined in a double olfactometer made of metal, glass, and filter-paper. A surprisingly great number of complete compensations were achieved with it.

If one type were taken of each of the nine complemented classes of LINNAEUS' classification of smell qualities, numerical values could be established for $\frac{72}{3} = 36$ combinations¹⁾. Afterwards J. HERMANIDES²⁾ did the same in his thesis for a doctor's degree. With three combinations his results coincided with mine and with those of a third observer (HERINGA). Since then I examined terpineol, guaiacol and valerianic acid chiefly with these odours in paraffin solutions.

Much greater accuracy together with sufficient persistence can be secured, when replacing paraffin solutions by a saturated aqueous solution in which there is a slight excess of odorous matter. The olfactometer then contains a system of phases, viz. air, water, odorous matter, which after a few days will be equilibrated and which moreover maintains its equilibrium against the adsorption of the filter-paper.

¹⁾ H. ZWAARDEMAKER, ü. d. Proportionen der Geruchscompensation, Arch. f. Anat. u. Physiology. 1907, Suppl. p. 60.

²⁾ Utrecht 1909. See also Proc. Roy. Ac. Amst. May 29 1909. Vol. 18, p. 53.

It will be well though, to take caproic acid instead of valerianic acid, the latter being too soluble and also lowering the surface-tension to such an extent that in less than .10 time it spreads over all surfaces that are moist at all. The persistent adsorption largely encumbers the technical conduct of the experiments. Generally speaking adsorption is a serious impediment in odorimetry, whatever method may be followed. With caproic acid its influence is felt far less than with valerianic acid.

The stimulus limen of my olfactory organ is for terpineol at about 1 mm. of the cylinder-length; for guaiacol at about 2 mm.; for caproic acid at about 1 mm. on the double olfactometer just described. The terpineol limen corresponds with 4 micrograms per litre of air, that of guaiacol with $\frac{1}{20}$ microgram, that of caproic acid with $\frac{1}{200}$ microgram (1 microgram = 1.10^{-6} gram).

The odorometrical coefficients ¹⁾ of the saturated solutions are respectively 10, 5 and 10, i. e. the smell stimuli, evoked by means of the olfactometer and expressed in the centimeters to which the cylinders have been moved out, must be multiplied respectively by 10, 5 and 10 to ascertain the number of "olfacts" with which they correspond.

The compensation-point is arrived at when in the double olfactometer the odorous cylinders are pushed off the inhaling tubes over lengths that stand to each other:

for terpineol and guaiacol,	as 4 cm. to 5 cm.
„ „ caproic acid „	1 „ „ 3 „
„ guaiacol „ „ „	1 „ „ 1 „

A somewhat greater length of one odorous cylinder makes its smell come to the front and vice versa. Equilibrium is also found with multiples of the proportions, though a weak antagonism sometimes occurs.

When mixing in the same proportions the saturated solutions that are decanted off into a separator, we obtain mixtures none of which will be inodorous, as stated above. It is true, their scent is considerably weaker than that of the original concentrated solutions from which they have been derived. The odorimetrical coefficients proved to be:

for the terpineol-guaiacol liquid mixt.	3—4
„ „ „ -caproic acid „	2 $\frac{1}{2}$
„ „ guaiacol- „ „ „	2

all being obviously smaller than the coefficients found for each of the constituents (terpineol 10, guaiacol 5, caproic acid 10).

¹⁾ H. ZWAARDEMAKER, *Physiol. d. Geruchs*, Leipzig, 1895 p. 185.

The electrifying power¹⁾ on the other hand proved to be additive.

The maximal charge of the single solutions, determined by Mr. VAN DER BIJL²⁾ appears to be per c.c. of sprayed solution:

<i>Terpineol.</i>	<i>Guaiacol.</i>	<i>Caproic acid.</i>
$\frac{1}{2}$ sat. (too great)	$\frac{1}{2}$ sat. 135.10^{-10} Coul.	$\frac{1}{2}$ sat. 196.10^{-10} Coul.
$\frac{1}{4}$ „ 182.10^{-10} Coul.	$\frac{1}{4}$ „ 57. „ „	$\frac{1}{4}$ „ 128. „ „

For the mixtures the charge per c.c. of sprayed solution is:

		Critical dist. (for 0.9 cc.)	Charge (per c.c.)
Terpineol-Guaiacol mixt.	(4 : 5)	60 c.m.	168.10^{-10} Coul.
Terpineol-Caproic acid mixt.	(1 : 2)	230 „	206. „ „
Guaiacol-Caproic acid mixt.	(1 : 1)	260 „	241. „ „

Regarding merely the odorous substances and neglecting the water the charge of the mixture would be too small; turning our attention to the water only and regarding the odorous substances merely as catalytic means, largely enhancing the initial ionization of the water, it would not be enough. The truth lies no doubt midway, since both the added odorous substances and the water are essential to bring about the electrical phenomenon, as measured by us.

But in whatever way the quantitative measurement may be carried out, the electrical phenomenon is at all events additive, whereas the olfactory quality appears to be weaker (weakened in the liquid mixture, faded out altogether in the mixture of the odorous gases in the double olfactometer).

From the foregoing it follows that in practice we are repeatedly confronted with fragrant matter of slight intensity, but of high electrifying power, when it is resolved in water and sprayed into a vapour. This will be the case, when it is built up of odorous substances which, when mixed, counteract each other in part, as to smell, but whose electrical effect is added together.

When the mixed substances pass into a chemical combination it

¹⁾ H. ZWAARDEMAKER, The Electrical Phenomenon in cloudlike condensed odorous Watervapours, examined in collaboration with Messrs H. KNOOPS and M. N. VAN DER BIJL, see These Proceedings Vol. XIX p. 44. The electrical phenomenon of odorous substances is allied to, but not identical with waterfall-electricity, for, apart from quantitative differences, our electrical phenomenon largely increases with a rise of temperature, whereas, according to LENARD, waterfall-electricity increases but little, and moreover the addition of salt augments vapour-electricity, whereas it diminishes true waterfall-electricity.

²⁾ All determinations were performed at an overpressure of two atm. with an earthed sprayer and at a critical distance. The latter was, with a spraying of 0.8 c.c. for $\frac{1}{2}$ dil. terpineol solution 4 c.c.; for $\frac{1}{2}$ dil. guaiacol solution 10 c.c.; for $\frac{1}{2}$ dil. caproic acid solution 13 c.c.

is a different matter. Take e.g. acetic acid and anilin, both of a rather high electrifying power; when they are combined to acetanilid (antifebrin) we get an odourless substance. Will it have electrifying power? To this question no a priori answer can be given, for the compound molecule as a whole and not the components from which it is derived, is answerable for the electrical phenomenon. Such a molecule, if electrifying at all, should satisfy the following conditions:

1. it should be soluble in water (substances insoluble in water do not give a charge).

2. it should lower the surface-tension of water, i. e. if a solid, it should yield the camphor-phenomenon.

3. it should volatilise from the aqueous solution, when spread over a large evaporation area.

The first and third conditions are fulfilled by acetanilid; experiments also show that it belongs to the remarkable group of organic substances, which like odorous substances produce the electrical phenomenon.

The three conditions just mentioned must be fulfilled in order to bring about an electrical phenomenon. Such substances may be odorous and *will* be so when moreover:

4. the substance is soluble in lipoid (*all* odorous substances are soluble in oil).

5. an odoriphore is present in the molecule.

The fourth condition is not or hardly satisfied by acetanilid; as to the fifth two groups of atoms are present in acetanilid that may be taken for odoriphores: 1. the aliphatic acid, 2. the anilin group.

RUPE and v. MAJEWSKI¹⁾ hold, however, that, when in one and the same molecule there are two odoriphores, a mutual counteraction may occur. This hypothesis and the slight solubility in oil account for the inodorousness of acetanilid. The same holds for other antipyretica (phenacetin, antipyrin, quinine). It is to be regretted that exceptions to such rules are never wanting.

All this leaves us still in the dark concerning the mysterious paralellism between smell, as a physiological, and vapour-electricity, as a physical property. This paralellism has thus far manifested itself for the vast majority of odorous substances:

a. in homologous series,

b. in the case of successive dilutions,

¹⁾ K. v. MAJEWSKI, Beitr. z. Kenntn. d. Diazo-imido-benzolderivate. Inaug. Diss. Basel 1898.

c. in the case of change of solubility and surface-tension through combining with salt- or sugar-solutions.

Divergencies are seen on either side. Some strong-smelling scents, moschus and sca σ tol, set up a sensation even in dilutions, the electrifying power being next to none. With antipyretica on the contrary, the smell-intensity is all but inappreciable, the electrifying power very considerable. For an interpretation we must, in the present stage of our research, look to the five conditions, just mentioned, upon the fulfilment of which the properties depend. Maybe the study of the dielectric-constant will throw some more light on the subject in connection with A. COEHN's theory of contact-electricity, according to which the difference of potential, in the case of mutual contact of two substances is proportional to the difference of the dielectric constants ¹⁾. The differences between the dielectric-constants of odorous substances and those of water are generally very great, so that likewise we may look for great charges on numberless droplets, when odorous molecules accumulate on their surfaces in virtue of the fall of the surface-tension. The rapid evaporation from the measureless area makes these differences all the more probable, especially when a slight rise of the temperature increases the evaporation and the sprayer is placed at the proper distance from the intercepting screen.

Chemistry. -- "*The equilibrium solid-liquid-gas in binary systems which present mixed crystals*". (*Fourth communication*). By Prof. H. R. KRUYT. (Communicated by Prof. ERNST COHEN).

(Communicated in the meeting of September 30, 1916.)

I. In the former communication ²⁾ has been communicated a research of Dr. W. D. HELDERMAN and myself on the three-phase equilibrium solid-liquid-gas (S L G) in the system bromine-iodine. The three-phase line exhibited in its PT-projection two maxima and one minimum, a peculiarity which is closely connected with the appearance of the compound IBr. For the general knowledge of the binary systems it is not uninteresting to more closely consider these equilibria; all the more so because the appearance of two maxima and one minimum on the melting branch of a com-

¹⁾ A. COEHN u. U. RAYDT. Göttinger Nachrichte 1909 p. 263.

²⁾ Proc. Royal Ac. A'dam, Meeting, of June 1916.