to less than half its previous value. In the vicinity of their CURIE-points, *nickel* and *iron* evidently behave in a quite analogous manner with respect
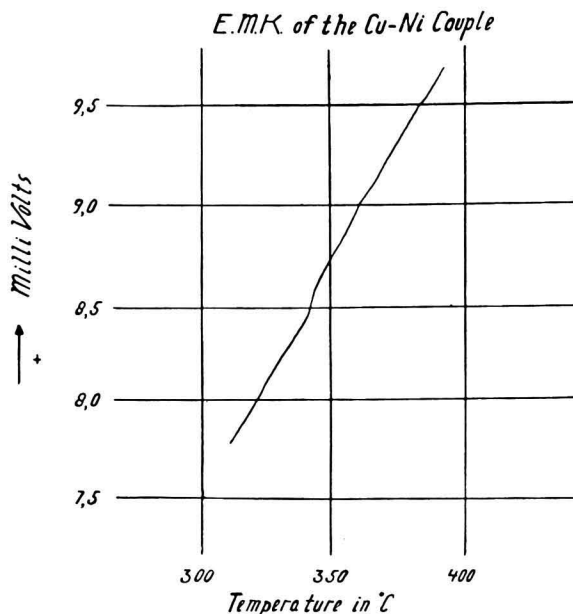

Fig. 5.   *Thermoelectrical Force: Ni—Cu.*

to their electrical resistances, as well as to their thermoelectrical properties towards *copper*.

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Physics. — *The most general photographic density-law.* By A. VAN KREVELD and L. S. ORNSTEIN, Utrecht. (Communication of the Dutch Foundation for photographic and cinematographic research).

I.   *Introduction.*

A photographic density-law is a relation between the intensity I of the light which falls on the photographic plate, the time of exposure t and the effect Z, caused by the exposure. Z may by either the developed density or the number of developed grains or any other measure for the photographic effect.

The following considerations are limited to the most important case

of exposures without intermittency effects. Then the general relation between I, t and Z can be written as follows:

$$\varphi (I, t, Z) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The first attempt to estimate this relation was that of BUNSEN and ROSCOE [1], who formulated the so-called reciprocity law:

$$\varphi (I \times t, Z) = 0 . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

According to this relation Z is a function of the product $I \times t$ (= the energy) only.

SCHWARZSCHILD [2] formulated the following law, which fitted his observations more exactly:

$$\varphi (I \times t^p, Z) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

p being a constant of the emulsion, the so-called SCHWARZSCHILD-exponent. But neither law could be confirmed by later investigators; p appeared to be a function of I and t. Therefore, the relation (3) is merely the general relation (1), p being equal to

$$- \left(\frac{\partial I}{\partial t} \right)_Z \times \frac{t}{I}. \quad \text{(See [3]).}$$

Besides (2) and (3) a number of other relations have been formulated in the course of time, most of them being purely empirical and containing several arbitrary constants. A well-known example is KRON's law:

$$\varphi (I \times t \times \sqrt{(\log I + a)^2 + 1}, Z) = 0 \quad . \quad . \quad . \quad . \quad (4)$$

which also failed to be confirmed in general [4].

In the last few years, however, some papers have been published, in which the relation (1) is compared for different wave-lengths and this comparison has led to some more fundamental relations, which, however, are less concrete than (2), (3) and (4).

II. *The three fundamental relations.*

Let λ be the wavelength, and let us denote the intensity of a monochromatic radiation of wavelength λ_i by I_i. Further let us denote the intensity of a non-monochromatic radiation by I_M.

If the mixture in question consists of the monochromatic radiations $\lambda_1, \lambda_2, \ldots \lambda_i \ldots \lambda_k$ we may write:

$$I_M = {}_1I_M + {}_2I_M + \ldots + {}_iI_M + \ldots + {}_nI_M = \sum_i {}_iI_M$$

${}_iI_M$ being the intensity (in the mixture) of the monochromatic component λ_i.

Then the following three relations hold for the range of normal exposures:

$$\log I_i - \log I_k = f_{ik}(Z). \qquad \text{(I)}$$

$$\sum_i \frac{{}_iI_M}{I_i} = 1 \qquad \text{(II)}$$

$$\log I_i = g_{ik}(t) \times \log I_k + h_{ik}(t). \qquad \text{(III)}$$

The relations I and II were discovered simultaneously. Relation I is the mathematical description of the fact (obtained by WEBB ([5]), and more generally deduced by VAN KREVELD ([3])) that the failure of the reciprocity law is equal for all wavelengths.

Relation II (obtained by VAN KREVELD ([3]), ([6]), see also WEBB ([7])) is the photographic addition-law, which permits the computation of the density-curve of a mixed colour from the density-curves of ist components.

Relation III (obtained by WEBB ([7])) means that the logarithmic density-curves of different wavelengths with the same time of exposure have a lineair relation to one another.

III. *Mathematical considerations.*

For the general case that $g_{ik} \overset{\ge}{\underset{\le}{=}} 1$ (for $g_{ik} \equiv 1$; see conclusion d) we may resolve $\log I_i$ from I and III:

$$\log I_i = \frac{h_{ik} - g_{ik} \times f_{ik}}{1 - g_{ik}}. \qquad \text{(5)}$$

We define:

$$\frac{h_{ik}}{1 - g_{ik}} \equiv H_{ik}(t)$$

$$\frac{g_{ik}}{1 - g_{ik}} \equiv G_{ik}(t)$$

so that:

$$\log I_i = H_{ik}(t) - G_{ik}(t) \times f_{ik}(Z). \qquad \text{(6)}$$

If we consider the relations I and III for another pair of colours e.g. λ_i and λ_l, we find in the same way:

$$\log I_i = H_{il}(t) - G_{il}(t) \times f_{il}(Z). \qquad \text{(7)}$$

From the comparison of (6) and (7) we conclude:

$$H_{ik} - G_{ik} \times f_{ik} \equiv H_{il} - G_{il} \times f_{il}. \qquad \text{(8)}$$

So the expression which is found for *log. I* does not depend on the second index and we may write:

$$log\, I_i = H_i\,(t) - G_i\,(t) \times f_i\,(Z) \quad . \quad . \quad . \quad . \quad (9)$$

From **I** we know that $f_{ik} \equiv -f_{ki}$;

From (6) and (9) we know: $f_i \equiv c_{ik} \times f_{ik}$.

Hence:

$$f_i \equiv c_{ik}\,f_{ik} \equiv -\,c_{ik}\,f_{ki} \equiv -\,\frac{c_{ik}}{c_{ki}}\,f_k \quad . \quad . \quad . \quad (10)$$

c_{ik} and c_{ki} being constants.

From (10) we learn that: $f_i\,(Z) \equiv c_i \times F\,(Z)$.

$F\,(Z)$ being independent of the wavelength. Thus we find from (9):

$$log\, I_i = H_i - G_i \times c_i \times F \quad . \quad . \quad . \quad . \quad (11)$$

In the same way:

$$log\, I_k = H_k - G_k \times c_k \times F \quad . \quad . \quad . \quad . \quad (12)$$

We subtract (12) from (11) and get:

$$log\, I_i - log\, I_k = H_i\,(t) - H_k\,(t) + \{G_k\,(t) \times c_k - G_i\,(t) \times c_i\} \times F\,(z) \quad . \quad (13)$$

If we compare (13) with **I** we find:

$$H_i\,(t) \equiv H_k\,(t) + d_{ik} \equiv H\,(t) + d_i$$
$$G_i\,(t) \times c_i \equiv G_k\,(t) \times c_k + e_{ik} \equiv G\,(t) + e_i$$

so that finally we get following relation (replacing *i* by λ):

$$\underline{log\, I_\lambda = H\,(t) + \{G\,(t) + e_\lambda\}\,F\,(Z) + d_\lambda} \quad . \quad . \quad . \quad (\mathbf{IV})$$

IV. *Conclusions.*

a. Relation **IV** is deduced from **I**, **II** and **III** purely mathematically: so it describes the observations without any hypothesis.

b. Only the two constants e_λ and d_λ are dependent on the wave-length. So the functions H, G and F are characteristic of the emulsion.

c. Relation **IV** can also be written in a non-logarithmic form:

$$I_\lambda = \delta_\lambda \times \vartheta\,(t) \times \varphi\,(Z)^{G(t)+e_\lambda} \quad . \quad . \quad . \quad . \quad (\mathbf{IVa})$$

If we substitute this expression in relation **II** we get a more general addition-law:

$$\sum_i \frac{{}_iI_M}{\delta_i \times \varphi\,(Z)^{e_i}} = \vartheta\,(t) \times \varphi\,(Z)^{G(t)} \quad . \quad . \quad . \quad . \quad (\mathbf{IIa})$$

Or, if we consider a continuous mixture of monochromatic radiations (e.g. sunlight) of the spectral intensity distribution $_\lambda I_M . d\lambda$, we obtain the following form:

$$\int_\lambda \frac{_\lambda I_M . d\lambda}{\delta_\lambda \times \varphi (Z)^{e\lambda}} = \vartheta (t) \times \varphi (Z)^{G(t)} \quad . \quad . \quad . \quad . \quad \textbf{(IIb)}$$

In the case of **IIa** we may put $_iI_M = q_i \times I_M$ and we find for the total intensity I_M the following law:

$$I_M = \vartheta (t) \times \varphi (Z)^{G(t)} \times \sum_i \frac{\delta_i}{q_i} \times \varphi (Z)^{c_i} \quad . \quad . \quad . \quad . \quad (14)$$

This form is only equivalent with **IVa** when c is constant, or in other words when the logarithmic density-curves of all wavelengths are parallel. In general this is not the case and then the form (14) is not equivalent to **IVa**.

We may draw the following conclusion:

The density-law for mixed colours is essentially different from that for monochromatic colours and has more complex mathematical properties.

Only in the case that the logarithmic density-curves for all monochromatic radiations are parallel to one another. the density-curves of all mixed colours are also parallel to them. This was already proved in an earlier paper ([8]). It is however, a degenerate case (see conclusion **d**).

d. The proof of **IV** was only correct for $g_{ik} \not\equiv 1$. When $g_{ik} \equiv 1$, the relation **III** is replaced by:

$$log\, I_i = log\, I_k + h_{ik} . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Combining this with **I** we obtain:

$$log\, I_i - log\, I_k = s_{ik} \qquad (s_{ik} \text{ being a constant}).$$

And **IV** is replaced by:

$$log\, I_\lambda = K (Z, t) + d_\lambda . \quad . \quad . \quad . \quad . \quad (16)$$

It is probable, however, though it cannot be proved from **I, II** and **III**, that in this case the following law holds:

$$log\, I_\lambda = H (t) + G (t) \times F (Z) + d_\lambda \quad . \quad . \quad . \quad . \quad (17)$$

e. It may be of some interest to compare relation **IV** with former density-laws. The reciprocity law (2) implies that:

$$H (t) \equiv - log\, t ; \quad G (t) \equiv 0.$$

SCHWARZSCHILD's law (3) implies:

$$H(t) \equiv -p \log t; \quad G(t) \equiv 0.$$

KRON's law (14) is not consistent with relation **IV**. At all events it is clear that $G(t)$ will be small and merely a correction-term.

V. *The most general density-law.*

We shall now consider monochromatic radiations only and emulsions for which $g_{ik} \not\equiv 1$.

Then then general relation **IV** holds:

$$\log I_\lambda = H(t) + \{G(t) + e_\lambda\} F(Z) + d_\lambda$$

We may ask now after the meaning of the individual terms of this expression.

The most simple term is d_λ. It has the dimensions of $\log I$ and is a wavelength-function which indicates the colour sensitivity of the emulsion. By choosing individual measures for the intensities of each wavelength, it may be cancelled.

The only function in **IV** which contains the photographic effect Z is F. It may be considered as the inverse of the logarithmic density-curve $Z = \varphi(\log I)$. The explicit form of the function F is not essentially important, as it can be altered arbitrarily by changing the measure of the photographic effect Z (e.g. density or opacity or number of developed grains or weight of the developed silver, etc.).

The wavelength-function e_λ is more important. It indicates how the steepness of the logarithmic density-curve depends on the wavelength and is independent of Z and t. On the other hand it is known that the wavelength-dependence of the steepness is caused by a combination of three essentially independent factors [9], so that we cannot expect a simple analytic form for the function e_λ.

Now only the functions $H(t)$ and $G(t)$ remain. They depend neither on the wavelength nor on the density and must have a fundamental meaning. It is possible and even probable that they have a simple analytic form and further there is a possibility that they are independent of the individual photographic emulsion, that means that they are characteristic of the photographic process in general. The experimental data known to us, however, do not permit more concrete conclusions to be drawn.

For practical purposes we can plot $\log I$ against $\log t$ (at constant density) and obtain a set of curves $\log I = R(\log t)$ with Z as parameter. Such sets have been published by several authors [10]. Now relation **IV** expresses that such a set must be a linear set, which means that all specimens of the set may be expressed as linear combinations of two of them. Hence:

$$R(\log t) = a R_1(\log t) + (1-a) R_2(\log t) \quad . \quad . \quad . \quad . \quad (18)$$

We tested this relation by the very extensive data of JONES, HUSE and HALL ([10]). They had investigated four different emulsions in a range of intensity of about $1 : 10^7$. From their tables 5—8 the *log I—log t*-curves can be easily calculated. The result of our test of relation (18) ist:

Emulsion	Range of densities considered in our calculation	Maximum deviation from relation (18) in $^0/_0$ of intensity
W. and W. panchomatic .	0.6—2.8	$4^0/_0$
Eastman Orthochromatic .	0.4—2.8	$4^0/_0$
Eastman Slow lantern .	0.2—3.0	$13^0/_0$
Process	0.2—2.8	$7^0/_0$

The numbers given in this table are the maximum deviations; the mean deviations are much smaller, so that we may say that relation (18) is fitted rigidly by the data of JONES, HUSE and HALL, while their own catenary-formula shows deviations up to a factor 10. We must acknowledge, however, that our relation (18) is not such an explicit form as the catenary-formula, so that it can be satisfied more easily. Further JONES, HUSE and HALL exposed with white light, while relation (18) was proved only for monochromatic light.

We also examined the data of ARENS and EGGERT ([10]). The general form of their sets of curves agrees with the supposition of a linear set (18) but, as the numerical data are not given, we could not make an exact comparison.

If we now consider the practical influence of the wavelength, relation **IV** expresses that *the linear set* (18) *must be the same for all wavelengths.*

A change of the wavelength only causes a shift of the individual curves of the set towards one another in the *log l*-direction.

<div align="center">**
*</div>

In conclusion we may say that, if the functions $H(t)$ and $G(t)$ are known explicitly, then *relation* **IV** *(or* **IVa***) is the most general density-law for monochromatic radiations and* **IIa** *(or* **IIb***) is the most general density-law for arbitrary radiations.*

All known laws (namely **I**, **II** and **III**) and all laws yet to be formulated must follow from **IIa** (or **IIb**) by specialization. In this way we have obtained the photographic analogon of the fundamental laws of thermodynamics, which indeed imply all special laws.

Finally we wish to make a remark about the function $F(Z)$. We already pointed out that this function has no fundamental meaning, on account of the latitude possible in choosing a measure for the photographic effect.

If it were possible, however, to choose a measure of fundamental significance — and this can only be the amount of silver of the latent image $F(Z)$ would obtain a physical meaning. So the methods EGGERT and NODDACK ([11]), which determine the amount of silver formed directly by the action of light, are important in this connection. The difficulty is that these methods can only be applied to exposures in the range of solarization, so that they are of no use for our problem, which refers to the range of normal exposures.

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Physics. — Remark to the paper: *The mechanism in the positive column of a discharge* (by L. S. ORNSTEIN, H. BRINKMAN and T. HAMADA). By L. S. ORNSTEIN and H. BRINKMAN. (Communication from the Physical Laboratory of the University of Utrecht).

(Communicated at the meeting of March 28, 1936).

In an appendix to the paper cited in the title (Cf. the Proceedings Febr. 1936) we have given an elementary deduction of the v. d. of electrons moving in a gas discharge with constant gradient. This deduction only holds true for the case that no excitation or ionization occurs. Now it is easy to generalize our deduction, so that also excitation and ionization are included.

Let us assume that above an energy ε_a the electron can excite the atom, losing in this process the energy ε_a. If now ε is the energy of the electron, the probability of excitation will be a function of $\varepsilon-\varepsilon_a-\gamma\,(\varepsilon-\varepsilon_a)$.