A STATISTICAL MOLECULAR THEORY OF ELECTRIC, MAGNETIC AND OPTICAL SATURATION PHENOMENA IN ISOTROPIC DIELECTRIC AND DIAMAGNETIC MEDIA

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It is the aim of the present investigation to establish a unified statistical-molecular theory of the nine electric, magnetic and optical saturation phenomena in isotropic dielectric and diamagnetic media (gases, condensed gases, liquids). For the case of a condensed medium composed of polar molecules of arbitrary symmetry, anisotropically polarizable and non-linearly deformable in an external field, general expressions yielding the nine molar constants have been derived, namely:

group I — the electric saturation: S_M^{ee} in an electric, S_M^{em} in a magnetic and S_M^{eo} in an optical field;

group II — the magnetic saturation: S_M^{me} in an electric, S_M^{mm} in a magnetic and S_M^{mo} in an optical field;

group III — the optical saturation: S_M^{oe} in an electric, S_M^{om} in a magnetic and S_M^{oo} in an optical field.

A discussion of these molar constants is given for particular cases of spherical and axial symmetry of the molecules. For axial symmetry, the general formulas reduce to those given previously. Moreover, expressions have been derived which relate the above-mentioned molar constants to the variations of the electric permittivity $\Delta\varepsilon^e$, $\Delta\varepsilon^m$, $\Delta\varepsilon^o$, of the magnetic permeability $\Delta\mu^e$, $\Delta\mu^m$, $\Delta\mu^o$, and of the optical refractive index Δn^e, Δn^m, Δn^o of the medium respectively, as resulting from the action thereon of a strong polarizing electric, magnetic or optical field. Only three of the nine possible effects under consideration have been detected to-date, namely, the electrooptical Kerr effect, the magneto-optical Cotton-Mouton effect and the electric saturation in an electric field, i. e. electro-electric saturation. The authors have derived equations for computing each of the six as yet unknown quantites $\Delta\varepsilon^m$, $\Delta\varepsilon^o$, ... Δn^o from the known experimental Kerr and Cotton-Mouton constants. By these formulas, the quantities $\Delta\varepsilon^m$, $\Delta\varepsilon^o$, ... Δn^o have been numerically computed for nitrobenzene.

1. *Introduction*

The electric, magnetic and optical properties of an isotropic medium are determined by the three scalar coefficients ε, μ and n characteristic of the substance. The electric permittivity ε and the magnetic permeability μ of the medium are measured applying an electric or magnetic field, respectively, which vary slowly, and whose frequency is much smaller than that of the Debye dispersion. The optical refractive index n is measured by an optical field, which is here understood to be the electric field of an electro-magnetic wave whose frequency exceeds that of the Debye dispersion. Such fields will be termed the electric $\boldsymbol{E}'$, magnetic $\boldsymbol{H}'$ and optical $\mathcal{E}'$ measuring field, respectively.

The present paper deals exclusively with dielectric, diamagnetic and isotropic media. Placed within one of these fields, the medium undergoes polarization of a kind corresponding to the measuring field and determined, respectively, by the vectors of electric polarization $\boldsymbol{P}^e$, magnetic polarisation $\boldsymbol{P}^m$ and optical polarisation $\boldsymbol{P}^o$. The relation between the electromagnetic material coefficients ε, μ and n, on the one hand and the vectors $\boldsymbol{P}^e, \boldsymbol{P}^m$ and $\boldsymbol{P}^o$ on the other, is given by the following general equations of electrodynamics:

$$\varepsilon - 1 = 4\pi \frac{\partial \boldsymbol{P}^e}{\partial \boldsymbol{E}'}, \quad \mu - 1 = 4\pi \frac{\partial \boldsymbol{P}^m}{\partial \boldsymbol{H}'}, \quad n^2 - 1 = 4\pi \frac{\partial \boldsymbol{P}^o}{\partial \mathcal{E}'}. \tag{1.1}$$

Usually, measuring fields $\boldsymbol{E}'$, $\boldsymbol{H}'$ and $\mathcal{E}'$ of small intensity are applied experimentally; as a result, each of the vectors $\boldsymbol{P}^e$, $\boldsymbol{P}^m$ and $\boldsymbol{P}^o$ in eqs. (1.1) is a linear function of the respective measuring field giving rise to the polarization, and the quantities ε, μ and n are functions which do not depend on the field, but depend solely on the medium and its thermodynamically determined state.

An entirely different picture is obtained if an additional external field of great intensity is applied, as e. g. a constant electric field $\boldsymbol{E}$. In this case, the polarization arising from the external field tends to saturation; the polarization vectors $\boldsymbol{P}^e$, $\boldsymbol{P}^m$ and $\boldsymbol{P}^o$ are now generally non-linear functions of the external field, whereas the electromagnetic material coefficients ε, μ and n now become functions (in at least the second degree) of the additionnally applied external electric field $\boldsymbol{E}$. This latter field will be termed the polarizing electric field.

The variations of the coefficients ε, μ and n as arising from the effect of a strong electric polarizing field $\boldsymbol{E}$ on the medium will be defined as follows:

$$\Delta\varepsilon^e = \varepsilon^e - \varepsilon, \quad \Delta\mu^e = \mu^e - \mu, \quad \Delta n^e = n^e - n, \tag{1.2}$$

wherein ε^e, μ^e and n^e denote the electric permittivity, magnetic permeability and optical refractive index of the medium, respectively, as measured in the presence of the polarizing field $\boldsymbol{E}$, whereas ε, μ and n denote the respective quantities as measured without a polarizing field (at $\boldsymbol{E} = 0$).

A constant magnetic field $\boldsymbol{H}$, or an optical field $\mathcal{E}$, may serve, too, as polarizing field; hence, the variations of ε, μ and n may be defined in analogy to those of eqs. (1.2) as brought about by a magnetic polarizing field $\boldsymbol{H}$:

$$\Delta\varepsilon^m = \varepsilon^m - \varepsilon, \quad \Delta\mu^m = \mu^m - \mu, \quad \Delta n^m = n^m - n, \tag{1.3}$$

or by a polarizing optical field $\mathcal{E}$:

$$\Delta\varepsilon^o = \varepsilon^o - \varepsilon, \quad \Delta\mu^o = \mu^o - \mu, \quad \Delta n^o = n^o - n. \tag{1.4}$$

Thus, a set of nine theoretically possible variations of the electromagnetic material coefficients ε, μ and n resulting from the effect of an external polarizing field $\boldsymbol{E}$, $\boldsymbol{H}$ or $\mathcal{E}$ are obtained, as shown in the following table:

polarizing field / measuring field	electric $\boldsymbol{E}$	magnetic $\boldsymbol{H}$	optical $\mathcal{E}$
electric $\boldsymbol{E}'$	$\Delta\varepsilon^e$	$\Delta\varepsilon^m$	$\Delta\varepsilon^o$
magnetic $\boldsymbol{H}'$	$\Delta\mu^e$	$\Delta\mu^m$	$\Delta\mu^o$
optical $\mathcal{E}'$	Δn^e	Δn^m	Δn^o

The variations defined in eqs. (1.2) — (1.4) will be termed, with respect to the coefficient measured, effects of electric ($\Delta\varepsilon^e$, $\Delta\varepsilon^m$, $\Delta\varepsilon^o$), magnetic ($\Delta\mu^e$, $\Delta\mu^m$, $\Delta\mu^o$) and optical (Δn^e, Δn^m, Δn^o) saturation. Strictly speaking, the effects $\Delta\varepsilon^e$, $\Delta\varepsilon^m$, ... etc. found experimentally did not represent the true saturation effect because of two by-effects appearing in the measurements. These are the reversible quadratic electro- or magneto-caloric and electro-or magnetostrictive effects. By computing both by-effects (see Piekara, Chełkowski and Kielich, 1957) and subtracting from the effect measured, e. g. $\Delta\varepsilon^e$, the true saturation effect is obtained, e. g.,

$$\Delta\varepsilon^e_{\text{sat}} = \Delta\varepsilon^e - \Delta\varepsilon^e_{\text{electrocal.}} - \Delta\varepsilon^e_{\text{electrostrict.}} \tag{1.5}$$

In the case of electric saturation, the by-effects are found to be small, of opposite sign, and nearly cancelling.

I. Effects of electric saturation

1. Electric saturation in an electric field, i. e. variation of the electric permittivity of the medium resulting from the effect of an electric polarizing field: $\Delta\varepsilon^e$.

The first experimental investigation was carried out by Herweg (1920), Kautzsch (1928) and others. Dipolar liquids, according to their particular properties, exhibit either „normal“ electric saturation i. e. a decrease in the electric permittivity ε under the effect of a strong electric field, $\Delta\varepsilon^e < 0$, or „inverse“ electric saturation, $\Delta\varepsilon^e > 0$, an effect first observed in nitrobenzene by one of the present authors (see A. Piekara and B. Piekara, 1936). This latter effect has but recently been proved to exist in some other dipolar liquids, owing to the considerable experimental difficulties involved (see A. Piekara and A. Chełkowski, 1956; A. Piekara, A. Chełkowski and S. Kielich, 1957; A. Chełkowski, 1958). Herweg (1920) was the first correctly to compute the electric saturation in dipolar gases from Debye's theory (1912). The theory was developed to account for anisotropic polar molecules by Debye (1925) and van Vleck (1932, 1937), and, subsequently, for molecules exhibiting non-linear deformation. by A. Piekara (1935, 1937). The theory accounting for polar liquids is due to Debye (1935), A. Piekara (1939 a, b, 1947, 1950), Peterlin and Stuart (1939), Anselm (1944), Frenkel (1946), Booth (1951), O'Dwyer (1951) Buckingham (1956 a), Schellman (1957) and the present authors (see A. Piekara and S. Kielich, 1957, 1958; S. Kielich, 1958). However, the effect of inverse electric saturation found in certain polar liquids is dealt with in the theories of the present authors (1939 a, b, 1950, 1957, 1958) and a mention thereof is made by Schellman (1957).

2. Electric saturation in a magnetic field, i. e. variation of the electric permittivity ε resulting from the effect of a magnetic polarizing field: $\Delta\varepsilon^m$.

This effect has not been observed experimentally in liquids; however, it has been shown to exist in liquid crystals by Jeżewski (1924, 1926, 1929) and Kast (1924, 1927). Experiments aimed at detecting this effect in pure liquids by one of the present authors and M. Schérer (1936) only settled an upper limit for $\Delta\varepsilon^m$. The theory for a paramagnetic gas is due to van Vleck (1932), and, for a diamagnetic gas of non-linearly deformable molecules — to A. Piekara (1935). Recently, the theory of this effect accounting for diamagnetic liquids was given by Buckingham (1957) and the present authors (A. Piekara and S. Kielich, 1957, 1958).

3. Electric saturation in an optical field, i. e. variation of the electric permittivity ε resulting from the effect of an optical polarizing field: $\Delta\varepsilon^o$.

As yet, this effect has not been experimentally detected. However, it is proved theoretically (see § 6, conclusion), that using modern pulse techniques, the effect could be made accessible to detection.

II. Effects of magnetic saturation

4. Magnetic saturation in an electric field, i. e. variation of the magnetic permeability μ resulting from the effect of an electric polarizing field: $\Delta\mu^e$.

The theory of this effect, for the case of a paramagnetic gas, was dealt with by van Vleck (1932), whereas that of diamagnetic liquids was the object of studies by Buckingham (1957).

5. Magnetic saturation in a magnetic field, i. e. variation of the permeability μ brought about by a polarizing magnetic field: $\Delta\mu^m$, and

6. Magnetic saturation in an optical field, i. e. variation of the permeability μ resulting from the effect of an optical polarizing field: $\Delta\mu^o$.

Neither of these effects has as yet been observed in dielectric and diamagnetic media, because of their extreme smallness.

III. *Effects of optical saturation*

7. Optical saturation in an electric field, i. e. variation of the optical refractive index n resulting from the effect of an electric polarizing field: Δn^e.

This effect is usually investigated in practice under the form of electric birefringence or Kerr's electrooptical effect (1875). The quantity Δn^e itself, which is known by the French term „retard absolu", is also the object of experimental investigation. Theories of Kerr's effect for gases are due to Voigt (1901), Langevin (1910), Born (1918, 1933), Gans (1921), Servant (1943, 1950) and Buckingham and Pople (1955, 1956), whilst theories dealing with the liquid state have been given by Müller (1936), Friedrich (1937), Piekara (1939, 1950), Peterlin and Stuart (1939), Anselm (1947), Buckingham (1955), Buckingham and Raab (1957), and the present authors (1957, 1958).

8. Optical saturation in a magnetic field, i. e. variation of the optical refractive index n resulting from the effect of a magnetic polarizing field: Δn^m.

It is the relative effect, i. e. the magnetic birefringence, as detected by Cotton and Mouton (1907), that is experimentally investigated. The theory of the Cotton-Mouton effect in liquids is due to Raman and Krishnan (1927), Piekara (1939, 1950), Peterlin and Stuart (1939), Snelman (1949), and Buckingham and Pople (1956).

9. Optical saturation in an optical field, i. e. variation of the optical refractive index n resulting from the effect of an optical field: Δn^o.

Recently, Buckingham (1956 b) pointed to the possibility of optical birefringence being induced in an isotropic medium by a light beam of very great intensity, and gave a theory of the effect. The latter, as yet, has not been observed in practice.

It is worth noting that, of the nine effects enumerated, only three, namely, the *first*, *seventh*, and *eighth* have been experimentally detected and investigated. The others still remain to be discovered.

The present authors have thus far published theories of five of these effects, namely a theory of electric saturation in an electric, magnetic and optical field and of the effects of Kerr and of Cotton-Mouton, respectively (A. Piekara and S. Kielich, 1957, 1958 a, b). The present paper brings a unified, statistical-molecular theory of all the nine effects for dielectric and diamagnetic isotropic media. The medium is, quite generally, assumed to be a condensed one, composed of anisotropic polar molecules of arbitrary symmetry, undergoing non-linear deformation in an external polarizing field. The interaction of the molecules of the medium is determined by intermolecular forces of an arbitrary nature. In the first place, the so-called molar constants of the various effects will be derived. In turn, the constants will be related to the variations of the quantities ε, μ and n given by eqs. (1.2) — (1.4). Finally, the variations of ε, μ and n in nitrobenzene in the six effects as yet not detected are numerically assessed.

The theory of all these effects, for anisotropic and polar molecules having the axial symmetry, was presented at the 7-th Colloque Ampère in Paris, 1958 (Piekara and Kielich, 1958 c).

2. *The molar constants of electric saturation*

Electric saturation in an electric field. Consider an isotropic medium of volume V containing N identical molecules. The spacial distribution of the molecules with respect to one another is given by the set of configurational variables $\tau = \tau(\boldsymbol{r}, \omega)$, with $\boldsymbol{r} = \{\boldsymbol{r}_1, \boldsymbol{r}_2, \dots \boldsymbol{r}_N\}$ denoting the positional variables and $\omega = \{\omega_1, \omega_2, \dots \omega_N\}$ — the orientational variables of the N molecules of the medium. The latter possess a permanent electric dipole moment and are electrically, magnetically and optically anisotropic.

Assume the medium under consideration is acted on simultaneously by an external electric maesuring field $\boldsymbol{E}'$ and an electric polarizing field $\boldsymbol{E}$. In general, the vectors subtend the angle Ω_{ee} given experimentally. The fields applied result in electric polarisation of the medium as a whole, residing in electric polarisation of the component molecules. As the medium is assumed to be a condensed one, the distances separating the molecules are small, and the latter, having undergone polarisation in the external field, interact by their total (i. e. permanent + induced) electric moments, giving rise to an additional internal field in the dielectric. This additional internal field superposes itself upon the external field to form the so called local field existing within each molecule of the dielectric.

Immersed in the local field, the molecules of the medium not only undergo linear polarisation (determined, in general, by a second order tensor), but are also subject to non-linear deformation (given by tensors of the third and fourth orders) consisting in deformation of the electronic shells and in some bending of the atomic bonds.

Hence, the total potential energy possessed by the arbitrary p-th molecule of the dielectric in the presence of the measuring $\boldsymbol{E}'$ and polarising $\boldsymbol{E}$ external electric fields is determined, in tensor notation, as follows:

$$\begin{aligned} u(\tau, \boldsymbol{E}', \boldsymbol{E})^{(p)} = u(\tau)^{(p)} &- \left(\mu_i^{(p)} F_{ei}^{(p)} + \frac{1}{2} a_{ij}^{e(p)} F_{ei}^{(p)} F_{ej}^{(p)} + \dots\right) - \\ &- \left(\bar{\mu}_i^{(p)} + a_{ij}^{e(p)} F_{ej}^{(p)} + \frac{1}{2} b_{ijk}^{ee(p)} F_{ej}^{(p)} F_{ek}^{(p)} + \dots\right) F_{ei}'^{(p)} - \\ &- \frac{1}{2}\left(\bar{a}_{ij}^{e(p)} + b_{ijk}^{ee(p)} F_{ek}^{(p)} + \frac{1}{2} c_{ijkl}^{ee(p)} F_{ek}^{(p)} F_{el}^{(p)} + \dots\right) F_{ei}'^{(p)} F_{ej}'^{(p)} - \dots, \end{aligned} \tag{2.1}$$

wherein $u(\tau)^{(p)}$ denotes the potential energy of the p-th molecule in the absence of the external fields ($\boldsymbol{E}' = \boldsymbol{E} = 0$), $\mu_i^{(p)}$ — the permanent electric dipole moment of the p-th molecule within the dielectric, $a_{ij}^{e(p)}$ — the electric polarizability tensor of the p-th molecule, and $b_{ijk}^{ee(p)}$, $c_{ijkl}^{ee(p)}$ — tensors determining the non-linear electro-electrical deformation of the p-th molecule of the medium, to be termed the tensors of electro-electrical deformability of the molecule. The above tensors are symmetrical in all summation indices i, j, k, l, which assume the values 1, 2, 3. $F_{ei}'^{(p)}$ and $F_{ei}^{(p)}$ denote the local electric measuring and polarizing fields, respectively, which act upon the p-th molecule of the dielectric.

The total electric dipole moment of the p-th molecule is given by the relation

$$m_i^e(\tau, \boldsymbol{E}', \boldsymbol{E})^{(p)} \equiv -\frac{du(\tau, \boldsymbol{E}', \boldsymbol{E})^{(p)}}{dF'^{(p)}_{ei}}, \tag{2.2}$$

which, with respect to eq. (2.1), may be rewritten as follows:

$$m_i^e(\tau, \boldsymbol{E}', \boldsymbol{E})^{(p)} = \mu_i^{(p)} + a_{ij}^{e(p)} F_{ej}^{(p)} + \frac{1}{2} b_{ijk}^{ee(p)} F_{ej}^{(p)} F_{ek}^{(p)} + \\ + \left(a_{ij}^{e(p)} + b_{ijk}^{ee(p)} F_{ek}^{(p)} + \frac{1}{2} c_{ijkl}^{ee(p)} F_{ek}^{(p)} F_{el}^{(p)} + \dots \right) F'^{(p)}_{ej} + \dots \tag{2.3}$$

The electric local fields $F'^{(p)}_{ei}$ and $F_{ei}^{(p)}$ in eqs. (2.1) and (2.3) acting on the p-th molecule of the dielectric consist of the external electric fields $\boldsymbol{E}'$ and $\boldsymbol{E}$, respectively, and of the internal field arising from the interaction of the molecules of the system with one another and with the external electric field. The problem, if restricted to dipole interactions, may be stated as follows

$$F'^{(p)}_{ei} = E'_i - \sum_{q=1}^{N} T_{ij}^{(pq)} m_j^{e(q)}, \quad F_{ei}^{(p)} = E_i - \sum_{q=1}^{N} T_{ij}^{(pq)} m_j^{e(q)}, \tag{2.4}$$

with $m_j^{e(q)}$ denoting the electric dipole moment of the q-th molecule given by eq. (2.3), and

$$T_{ij}^{(pq} = \frac{1}{r_{pq}^5} (r_{pq}^2 \delta_{ij} - 3 r_{pqi} r_{pqj}) \tag{2.4a}$$

— the dipole interaction tensor, non-vanishing for $p \neq q$ and vanishing for $p = q$, $\boldsymbol{r}_{pq} = \boldsymbol{r}_q - \boldsymbol{r}_p$ — the vector connecting the centers of the p-th and q-th molecules ($\boldsymbol{r}_p$ and $\boldsymbol{r}_q$ being their radii-vectors) and δ_{ij} — the unit tensor,

$$\delta_{ij} = \begin{cases} 1 \text{ for } i = j, \\ 0 \text{ for } i \neq j. \end{cases} \tag{2.4b}$$

The next fundamental point of the theory is to calculate the component in the direction of the external electric measuring field, $\boldsymbol{E}'$, of the vector of the electric polarisation $\boldsymbol{P}^e$ arising in the dielectric from the effect of fields $\boldsymbol{E}'$ and $\boldsymbol{E}$, which will be denoted by $P_{E'}^e$. Applying statistical mechanics to calculate $P_{E'}^e$, and accounting for the fact that the dielectric consists of N molecules of one kind, one may write

$$P_{E'}^e = \frac{N}{V} \langle m_{E'}^e \rangle_{E',E}, \tag{2.5}$$

wherein

$$m_{E'}^e = m_i^e(\tau, \boldsymbol{E}', \boldsymbol{E})^{(p)} \alpha'^{(p)}_i \tag{2.5a}$$

is the component of the electric moment of the molecule in the direction of the measuring field $\boldsymbol{E}'$, whereas $m_i^e(\tau, \boldsymbol{E}', \boldsymbol{E})$ denotes the electric moment of the p-th molecule given by eq. (2.3), and the $\alpha_i^{'(p)}$ are the directional cosines of the angles subtended by the axes of the molecular reference system attached to the p-th molecule and the direction of the measuring field $\boldsymbol{E}'$.

The symbol $\langle m^e_{E'} \rangle_{E',E}$ in eq. (2.5) serves to indicate the mean statistical value of the quantity $m^e_{E'}$, computed when the dielectric immersed in the external fields $\boldsymbol{E}'$ and $\boldsymbol{E}$ is in thermodynamical equilibrium. By classical statistical mechanics, for a condensed medium, $\langle m^e_{E'} \rangle_{E',E}$ is defined as follows:

$$\langle m^e_{E'} \rangle_{E',E} = \frac{\int\int\ldots\int m_i^e(\tau, \boldsymbol{E}', \boldsymbol{E})^{(p)}\, \alpha_i^{'(p)}\, e^{-\frac{\sum_{p=1}^{N} u(\tau, \boldsymbol{E}', \boldsymbol{E})^{(p)}}{kT}}\, d\tau_1\, d\tau_2 \ldots d\tau_N}{\int\int\ldots\int e^{-\frac{\sum_{p=1}^{N} u(\tau, \boldsymbol{E}', \boldsymbol{E})^{(p)}}{kT}}\, d\tau_1\, d\tau_2 \ldots d\tau_N} \tag{2.6}$$

wherein k denotes Boltzmann's constant, T — the Kelvin temperature of the system, $d\tau_p$ — the element of the configurational space of the p-th molecule of the system; $\sum_{p=1}^{N} u(\tau, \boldsymbol{E}'\, \boldsymbol{E})^{(p)}$ with $u(\tau, \boldsymbol{E}'\, \boldsymbol{E})^{(p)}$ from eq. (2.1) denotes the total potential energy of the system in the presence of the fields $\boldsymbol{E}'$ and $\boldsymbol{E}$. In the absence of the external fields, $\sum_{p=1}^{N} u(\tau, o)^{(p)} = U_N$ is the potential energy of interaction of the N molecules of the medium. In general, U_N consists of the Lennard-Jones potential, the London dispersive forces, the energy of the dipolar (Keesom) and inductive (Debye-Falkenhagen) interaction of the molecules, and of multipole molecular interaction of various other kinds.

The calculation of $\langle m^e_{E'} \rangle_{E',E}$, as defined by eq. (2.6) together with eqs. (2.1) and (2.3), wherein the local fields are given by eq. (2.4), is generally a rather involved problem, and, in fact, can be solved for the linear effects of dielectric polarisation and refraction (see Kirkwood (1936), Fuller-Brown (1950), De Boer, Maasen and Seldam (1953), Harris (1955), Buckingham and Pople (1955), Mandel and Mazur (1958)). In computing the non-linear effects, it is necessary to introduce simplifications; thus, in place of eq. (2.4), the following relations will be assumed:

$$F_{ei}^{'(p)} = F'_e\, \alpha_i^{'(p)}, \qquad F_{ei}^{(p)} = F_e\, \alpha_i^{(p)}, \tag{2.7}$$

wherein F'_e and F_e denote the mean local electric fields not depending directly on the configuration of the molecules, and $\alpha_i^{'(p)}$, $\alpha_i^{(p)}$ — the cosines of the angles subtended by the direction of these fields and the axes of the reference system attached to the p-th molecule of the dielectric.

Substitution of eqs. (2.1) and (2.3) together with (2.7) in (2.6), expansion in powers of the fields F'_e and F_e and averageing over all possible positions of the p-th molecule with respect to the direction of the measuring field yields (see Appendix):

$$\begin{aligned} \langle m^e_{E'} \rangle_{E',E} = \frac{1}{3} \left(a^e_{ij} \delta_{ij} + \frac{\mu_i \, \mu_j}{kT} \left\langle \sum_q \omega^{(pq)}_{ij} \right\rangle \right) F'_e + \\ + \frac{1 + 2\cos^2 \Omega_{ee}}{90} \left\{ 3 c^{ee}_{ijkl} \, \delta_{ij} \, \delta_{kl} + \frac{12 \mu_i \, b^{ee}_{jkl}}{kT} \left\langle \sum_q \omega^{(pq)}_{ij} \, \delta_{kl} \right\rangle + \right. \\ + \frac{2 a^e_{ij} \, a^e_{kl}}{kT} \left\langle \sum_q (3 \omega^{(pq)}_{ik} \, \omega^{(pq)}_{jl} - \delta_{ij} \, \delta_{kl}) \right\rangle + \\ + \frac{4 a^e_{ij} \, \mu_k \, \mu_l}{k^2 \, T^2} \left\langle \sum_{qr} (3 \omega^{(pq)}_{ik} \, \omega^{(pr)}_{jl} - \delta_{ij} \omega^{(qr)}_{kl}) \right\rangle + \\ \left. + \frac{\mu_i \, \mu_j \, \mu_k \, \mu_l}{k^3 \, T^3} \left(3 \left\langle \sum_{qrs} \omega^{(pq)}_{ij} \, \omega^{(rs)}_{kl} \right\rangle - 5 \left\langle \sum_q \omega^{(pq)}_{ij} \right\rangle \left\langle \sum_{rs} \omega^{(rs)}_{kl} \right\rangle \right) \right\} F'_e \, F^2_e, \end{aligned} \tag{2.8}$$

wherein the $\omega^{(pq)}_{ij}$ are the cosines of the angles between the i-th axis of the molecular system of reference attached to the p-th molecule and the j-th axis of that attached to the q-th, Ω_{ee} — the angle between the electric measuring field vector $\boldsymbol{E}'$ and the vector $\boldsymbol{E}$ of the polarizing field. The mean values denoted by the symbol $< >$ without subscripts are those computed in the absence of the external fields ($\boldsymbol{E}' = \boldsymbol{E} = 0$). Thus

$$\langle \Phi \rangle = \frac{\int\int \dots \int \Phi(\tau) \, e^{-\frac{U_N}{kT}} \, d\tau_1 \, d\tau_2 \dots d\tau_N}{\int\int \dots \int e^{-\frac{U_N}{kT}} \, d\tau_1 \, d\tau_2 \dots d\tau_N} \tag{2.9}$$

is the mean statistical value of the function $\Phi(\tau)$ in the absence of the external fields.

In eq. (2.8), the directional cosines $\omega^{(pq)}_{ij}$, ... $\omega^{(rs)}_{kl}$ fixing the orientation of the axes of different molecular reference systems with respect to one another still remain to be statistically averaged, account being taken of the various types of molecular interaction implicit in the potential energy U_N. This may be effected by the definition of eq. (2.9) for special cases if the symmetry and structure of the molecules making up the dielectric are known.

With the statistical mean $\langle m^e_{E'} \rangle_{E',E}$, it is possible to compute the quantity termed "molar constant of electric saturation in a polarizing electric field" and defined as follows:

$$S^{ee}_M \equiv \frac{4\pi}{3} \frac{N_A}{F^2_e} \left\{ \frac{\partial}{\partial F'_e} \langle m^e_{E'} \rangle_{E',E} - \left(\frac{\partial}{\partial F'_e} \langle m^e_{E'} \rangle_{E',E} \right)_{E=0} \right\}, \tag{2.10}$$

N_A being Avogadro's number.

The definition (2.10) of the molar constant of electro-electric saturation S^{ee}_M

together with eq. (2.8) yields

$$
\begin{aligned}
S_M^{ee} = \frac{2\pi N_A}{135}(1+2\cos^2\Omega_{ee})\Bigg\{ & 3c_{iijj}^{ee} + \frac{12\mu_i b_{jkl}^{ee}}{kT}\left\langle\sum_q \omega_{ij}^{(pq)}\delta_{kl}\right\rangle + \\
& + \frac{2a_{ij}^{e} a_{kl}^{e}}{kT}\left\langle\sum_q (3\omega_{ik}^{(pq)}\omega_{jl}^{(pq)} - \delta_{ij}\delta_{kl})\right\rangle + \\
& + \frac{4a_{ij}^{e}\mu_k\mu_l}{k^2T^2}\left\langle\sum_{qr}(3\omega_{ik}^{(pq)}\omega_{jl}^{(pr)} - \delta_{ij}\omega_{kl}^{(qr)})\right\rangle + \\
& + \frac{\mu_i\mu_j\mu_k\mu_l}{k^3T^3}\left(3\left\langle\sum_{qrs}\omega_{ij}^{(pq)}\omega_{kl}^{(rs)}\right\rangle - \left\langle\sum_q \omega_{ij}^{(pq)}\right\rangle\left\langle\sum_{rs}\omega_{kl}^{(rs)}\right\rangle\right)\Bigg\}. \qquad (2.11)
\end{aligned}
$$

The molar constant is, in general, given correctly by eq. (2.11) for condensed dielectrics (condensed gases and liquids) composed of polar molecules of one kind possessing symmetry of an arbitrary type and non-linearly deformable in an external electric field. In the case of a gas, the potential energy of molecular interaction may be neglected ($U_N = 0$); the statistical mean values of eq. (2.9) then reduce to isotropic averages, and the following molar constant ${}_{gas}S_M^{ee}$ is obtained for a gas:

$$
\begin{aligned}
{}_{gas}S_M^{ee} = \frac{2\pi N_A}{135}(1+2\cos^2\Omega_{ee})\Bigg\{ & 3c_{iijj}^{ee} + \frac{12}{kT}\mu_i b_{ijj}^{ee} + \\
& + \frac{2}{kT}(3a_{ij}^{e}a_{ij}^{e} - a_{ii}^{e}a_{jj}^{e}) + \frac{4}{k^2T^2}(3a_{ij}^{e}\mu_i\mu_j - a_{ii}^{e}\mu_j^2) - \frac{2}{k^3T^3}\mu_i^3\mu_j^2\Bigg\}. \qquad (2.12)
\end{aligned}
$$

The discussion of the equations derived above will begin with that of eq. (2.12) for gases. The first term therein, $3\,c_{iijj}^{ee}$, is temperature-independent and accounts for a purely deformational effect consisting in immediate deformation of the molecules of the dielectric by the external polarizing field $\boldsymbol{E}$. This effect may be derived directly from eqs. (2.3), (2.5a) and (2.7) by isotropic averageing only. The second term, $12\,\mu_i\,b_{ijj}^{ee}\,(kT)^{-1}$, which is a deformational-dipolar one, is temperature-dependent and accounts for the deformational-orientational effect originally computed for gases by one of the present authors (A. Piekara, 1935, 1937 a b). The remaining temperature-dependent terms, namely: the purely anisotropic term $2(3\,a_{ij}^{e}a_{ij}^{e} - a_{ii}^{e}a_{jj}^{e})(kT)^{-1}$, the anisotropic-dipolar term $4(3\,a_{ij}^{e}\mu_i\mu_j - a_{ii}^{e}\mu_j^2)(kT)^{-2}$ and the purely dipolar term $2\,\mu_i^2\,\mu_j^2\,(kT)^{-3}$, determine the effect of molecular orientation originally computed for gases by Debye (1925). This effect had already been introduced into the theory of the phenomenon of Kerr and of Cotton-Mouton by Langevin (1910) for molecules exhibiting anisotropy only, and by Born (1918) for anisotropic and polar molecules. The effect of molecular orientation consists in the following: the molecules of the dielectric tend to an orientation in which the axis of their permanent dipole moment and that of their greatest polarizability are parallel to the direction of the electric field applied, an effect that is counteracted by the unordered, thermal motion of the molecules. This results in a state of thermodynamical-statistical equilibrium in which the molecules attain a degree of ordering, the privileged direction being that of the external electric polarizing field.

It will be seen from eq. (2.11) for dielectric liquids that the above effects, with the exception of the purely deformational effect, are intimately related with the molecular interaction existing throughout the dielectric. The latter, in general, is determined by the mean statistical values of various functions of the directional cosines $\omega_{ij}^{(pq)}$ of the angles between the axes of the molecular systems of reference attached to the p-th and to the q-th molecule of the medium. The deformational effects are generally insignificant and may be neglected in considering polar liquids. In weakly polar liquids, whose polarizability is strongly anistropic, the purely anisotropic term, and especially the anisotropic-dipolar term, become important. On the other hand, in strongly polar liquids, it is the purely dipolar term and the characteristic effect of molecular interaction related thereto that play the decisive part; if the energy of molecular interaction is sufficiently great, this effect leads to the change in the sign of $\Delta\varepsilon^e$, as experimentally observed. No such change in the sign of $\Delta\varepsilon^e$ is predicted by eq. (2.12), which holds for gases, and wherein the molecular interaction is not accounted for (see A. Piekara, 1939, 1950; A. Piekara and S. Kielich, 1957, 1958). The discussion of eqs. (2.11) and (2.12) with respect to the symmetry of the molecule will be continued in § 5.

Electric saturation in a magnetic field. Consider a system subjected simultaneously to the effect of an electric measuring field $\boldsymbol{E}'$ and to that of a magnetic polarizing field $\boldsymbol{H}$.

The potential energy of the p-th molecule of the diamagnetic medium is now given by

$$u(\tau, \boldsymbol{E}', \boldsymbol{H})^{(p)} = u(\tau)^{(p)} - \frac{1}{2}\, a_{ij}^{m(p)}\, F_{mi}^{(p)}\, F_{mj}^{(p)} - \\ - \left(\mu_i^{(p)} + \frac{1}{2}\, b_{i,jk}^{em(p)}\, F_{mj}^{(p)}\, F_{mk}^{(p)} + \ldots\right) F_{ei}^{\prime(p)} - \\ - \frac{1}{2}\left(a_{ij}^{e(p)} + \frac{1}{2}\, c_{ij,kl}^{em(p)}\, F_{mk}^{(p)}\, F_{ml}^{(p)} + \ldots\right) F_{ei}^{\prime(p)}\, F_{ej}^{\prime(p)} - \ldots, \tag{2.13}$$

wherein $a_{ij}^{m(p)}$ is the magnetic polarizability tensor of the p-th molecule, $b_{i,jk}^{em(p)}$ and $c_{ij,kl}^{em(p)}$ — the tensors of its magneto-electric deformability, and $F_{mi}^{(p)}$ — the local polarizing magnetic field acting on the p-th molecule of the system. The tensor $a_{ij}^{m(p)}$ is symmetrical in the indices i, j, the tensor $b_{i,jk}^{em(p)}$ — in j, k, and the tensor $c_{ij,kl}^{em(p)}$ — in the separate pairs of indices i, j and k, l.

By eq. (2.13), the following expression is obtained for the electric moment of the p-th molecule in the presence of the fields $\boldsymbol{E}'$ and $\boldsymbol{H}$:

$$m_i^e(\tau, \boldsymbol{E}', \boldsymbol{E})^{(p)} = \mu_i^{(p)} + \frac{1}{2}\, b_{i,jk}^{em(p)}\, F_{mj}^{(p)}\, F_{mk}^{(p)} + \\ + \left(a_{ij}^{e(p)} + \frac{1}{2}\, c_{ij,kl}^{em(p)}\, F_{mk}^{(p)}\, F_{ml}^{(p)} + \ldots\right) F_{ej}^{\prime(p)} + \ldots \tag{2.14}$$

As previously, the statistical average $\langle \overset{e}{m}_{E'} \rangle_{E',H}$ is computed from eqs. (2.13) and (2.14), and a definition quite similar to that given by eqs. (2.10) yields the molar constant of electric saturation in a magnetic field (molar constant of magneto-electric saturation) as follows:

$$S_M^{em} = \frac{2\pi N_A}{135} \Bigg\{ 5 \left(c^{em}_{ii,jj} + \frac{2\mu_i\, b^{em}_{j,kl}}{kT} \left\langle \sum_q \omega^{(pq)}_{ij}\, \delta_{kl} \right\rangle \right) +$$

$$+ (3\cos^2 \Omega_{em} - 1) \Bigg[3c^{em}_{ij,ij} - c^{em}_{ii,jj} + \frac{2\mu_i\, b_{j,kl}}{kT} \left\langle \sum_q (3\omega^{(pq)}_{ik}\, \delta_{jl} - \omega^{(pq)}_{ij}\, \delta_{kl}) \right\rangle +$$

$$+ \frac{\overset{e}{a}_{ij}\, \overset{m}{a}_{kl}}{kT} \left\langle \sum_q (3\omega^{(pq)}_{ik}\, \omega^{(pq)}_{jl} - \delta_{ij}\, \delta_{kl}) \right\rangle +$$

$$+ \frac{\overset{m}{a}_{ij}\, \mu_k\, \mu_l}{k^2\, T^2} \left\langle \sum_{qr} (3\omega^{(pq)}_{ik}\, \omega^{(pr)}_{jl} - \delta_{ij}\, \omega^{(qr)}_{kl}) \right\rangle \Bigg] \Bigg\}, \tag{2.15}$$

wherein Ω_{em} denotes the angle subtended by the vector of the electric measuring field ***E'*** and that of the polarizing magnetic field ***H***.

For a gas, this yields

$$_{gas}S_M^{em} = \frac{2\pi N_A}{135} \Bigg\{ 5\, (c^{em}_{ii,jj} + \frac{2}{kT}\, \mu_i\, b^{em}_{i,jj}) +$$

$$+ (3\cos^2 \Omega_{em} - 1) \Bigg[3\, c^{em}_{ij,ij} - c^{em}_{ii,jj} + \frac{2}{kT} (3\, \mu_i\, b^{em}_{j,ij} - \mu_i\, b^{em}_{i,jj}) +$$

$$+ \frac{1}{kT} (3\, \overset{e}{a}_{ij}\, \overset{m}{a}_{ij} - \overset{e}{a}_{ii}\, \overset{m}{a}_{jj}) + \frac{1}{k^2T^2} (3\, \mu_i\, \mu_j\, \overset{m}{a}_{ij} - \mu_i^2\, \overset{m}{a}_{jj}) \Bigg] \Bigg\}. \tag{2.16}$$

Electric saturation in an optical field. Assume the measuring field to be, as in the foregoing instances, a slowly varying electric field E', while the polarizing field is a rapidly varying electric field (whose frequency exceeds that of Debye dispersion), i. e. an optical field (excluding, however, frequencies within the range of optical absorption). The latter will be assumed to be sine variable: $\mathcal{E} = \mathcal{E}_a \cos 2\pi \nu t$, with $\mathcal{E}_a$ denoting the amplitude of the vector $\mathcal{E}$, ν — the frequency, and t — the time.

As the period ν^{-1} of the oscillations of the polarizing field is so short that the molecules are unable to keep pace with its variations, the "effective potential energy" and "effective electric moment" of a molecule of the medium are given by the mean values of (2.1) and (2.3) over an entire period of the oscillations of the polarizing electric field applied. The definition of the time mean value of a function of the time:

$$\widetilde{\Phi(t)} = \nu \int_0^{\frac{1}{\nu}} \Phi(t)\, dt \tag{2.17}$$

yields

$$\widetilde{\mathcal{E}_i} = \widetilde{\mathcal{E}_i \mathcal{E}_j \mathcal{E}_k} = 0, \qquad \widetilde{\mathcal{E}_i \mathcal{E}_j} = \frac{1}{2} \mathcal{E}_{ai} \mathcal{E}_{aj}\,, \tag{2.17a}$$

and eqs. (2.1) and (2.3), on averageing over the period with respect to the rapidly varying field, take the form:

$$\begin{aligned} \widetilde{u\,(\tau, \boldsymbol{E}', \mathcal{E})^{(p)}} &= u\,(\tau)^{(p)} - \frac{1}{2}\, a_{ij}^{0(p)}\, \widetilde{F_{oi}^{(p)}\, F_{oj}^{(p)}} - \\ &- (\mu_i^{(p)} + \frac{1}{2}\, b_{i,jk}^{eo(p)}\, \widetilde{F_{oj}^{(p)}\, F_{ok}^{(p)}} + \ldots)\, F_{ei}^{\prime(p)} - \\ &- \frac{1}{2}\, (a_{ij}^{e(p)} + \frac{1}{2}\, c_{ij,kl}^{eo(p)}\, \widetilde{F_{oj}^{(p)}\, F_{ok}^{(p)}} + \ldots)\, F_{ei}^{\prime(p)}\, F_{ej}^{\prime(p)} - \ldots \end{aligned} \tag{2.18}$$

and

$$\begin{aligned} \widetilde{m_i^e\,(\tau, \boldsymbol{E}', \mathcal{E})^{(p)}} &= \mu_i^{(p)} + \frac{1}{2}\, b_{i,jk}^{eo(p)}\, \widetilde{F_{oj}^{(p)}\, F_{ok}^{(p)}} + \\ &+ \left(a_{ij}^{e(p)} + \frac{1}{2}\, c_{ij,kl}^{eo(p)}\, \widetilde{F_{ok}^{(p)}\, F_{ol}^{(p)}} + \ldots\right) F_{ej}^{\prime(p)} + \ldots, \end{aligned} \tag{2.19}$$

wherein $a_{ij}^{o(p)}$ is the tensor of the optical polarizability of the p-th molecule, $b_{i,kl}^{eo(p)}$ and $c_{ij,kl}^{eo(p)}$ — the tensor of its optico-electrical deformability, and $F_{oi}^{(p)}$ — the optical local polarizing field acting upon the p-th molecule of the system. For an optically inactive substance, the tensor $a_{ij}^{o(p)}$ is symmetrical in the indices i, j, the tensor $b_{i,jk}^{eo(p)}$ — in the indices j, k, and $c_{ij,kl}^{eo(p)}$ — in the pairs of indices i, j and k, l. The statistical mean value of the component of the electric moment (2.19) in the direction of the measuring field $\boldsymbol{E}'$ is obtained from eqs. (2.18) and (2.19), using a method explained in the Appendix, in the form:

$$\begin{aligned} \widetilde{\langle m_{E'}^e \rangle}_{E',\mathcal{E}} &= \frac{1}{3} \left(a_{ij}^e\, \delta_{ij} + \frac{\mu_i \mu_j}{kT} \left\langle \sum_q \omega_{ij}^{(pq)} \right\rangle \right) F_e' + \\ &+ \frac{1}{90} \Bigg\{ 3\,(2 - \cos^2 \Omega_{eo}) \left(c_{ii,jj}^{eo} + \frac{2\mu_i\, b_{j,kl}^{eo}}{kT} \left\langle \sum_q \omega_{ij}^{(pq)}\, \delta_{kl} \right\rangle \right) + \\ &+ (3 \cos^2 \Omega_{eo} - 1) \Bigg[3\, c_{ij,ij}^{eo} + \frac{6\, \mu_i\, b_{j,kl}^{eo}}{kT} \left\langle \sum_q \omega_{ik}^{(pq)}\, \delta_{jl} \right\rangle + \\ &+ \frac{a_{ij}^e\, a_{kl}}{kT} \left\langle \sum_q (3\omega_{ik}^{(pq)}\, \omega_{jl}^{(pq)} - \delta_{ij}\, \delta_{kl}) \right\rangle + \\ &+ \frac{a_{ij}^o\, \mu_k\, \mu_l}{k^2\, T^2} \left\langle \sum_{qr} (3\omega_{ik}^{(pq)}\, \omega_{jl}^{(pr)} - \delta_{ij}\, \omega_{kl}^{(qr)}) \right\rangle \Bigg] \Bigg\}\, F_e'\, \widetilde{F_o^2}\,, \end{aligned} \tag{2.20}$$

with Ω_{eo} denoting the angle subtended by the vectors $\boldsymbol{E}'$ and $\mathcal{E}$.

The molar constant of electric saturation in an optical field is defined by

$$S_M^{eo} \equiv \frac{4\pi}{3}\frac{N_A}{\widetilde{F}_o^2}\left\{\frac{\partial}{\partial F'_e}\langle \widetilde{\overset{e}{m}_{E'}}\rangle_{E',\varepsilon} - \left(\frac{\partial}{\partial F'_e}\langle \widetilde{\overset{e}{m}_{E'}}\rangle_{E',\varepsilon}\right)_{\varepsilon=0}\right\}. \tag{2.21}$$

By (2.20), this yields

$$\begin{aligned} S_M^{eo} = \frac{2\pi N_A}{135}\Bigg\{5\left(c^{eo}_{ii,jj} + \frac{2\mu_i b^{eo}_{j,kl}}{kT}\left\langle\sum_q \omega^{(pq)}_{ij}\,\delta_{kl}\right\rangle\right) + \\ + (3\cos^2\Omega_{eo} - 1)\Bigg[3c^{eo}_{ij,ij} - c^{eo}_{ii,jj} + \frac{2\mu_i b^{eo}_{j,kl}}{kT}\left\langle\sum_q (3\omega^{(pq)}_{ik}\,\delta_{jl} - \omega^{(pq)}_{ij}\,\delta_{kl})\right\rangle + \\ + \frac{\overset{e}{a}_{ij}\,\overset{o}{a}_{kl}}{kT}\left\langle\sum_q (3\omega^{(pq)}_{ik}\,\omega^{(pq)}_{jl} - \delta_{ij}\,\delta_{kl})\right\rangle + \\ + \frac{\overset{o}{a}_{ij}\,\mu_k\,\mu_l}{k^2\,T^2}\left\langle\sum_{qr} (3\omega^{(pq)}_{ik}\,\omega^{(pr)}_{jl} - \delta_{ij}\,\omega^{(qr)}_{kl})\right\rangle\Bigg]\Bigg\}. \end{aligned} \tag{2.22}$$

For a gas, the foregoing equation reduces to

$$\begin{aligned} {}_{\text{gas}}S_M^{eo} = \frac{2\pi N_A}{135}\Bigg\{5\left(c^{eo}_{ii,jj} + \frac{2}{kT}\,\mu_i\,b^{eo}_{i,jj}\right) + \\ + (3\cos^2\Omega_{eo} - 1)\Bigg[3c^{eo}_{ij,ij} - c^{eo}_{ii,jj} + \frac{2}{kT}\,(3\mu_i\,b^{eo}_{j,ij} - \mu_i\,b^{eo}_{i,jj}) + \\ + \frac{1}{kT}\,(3\overset{e}{a}_{ij}\,\overset{o}{a}_{ij} - \overset{e}{a}_{ii}\,\overset{o}{a}_{jj}) + \frac{1}{k^2\,T^2}\,(3\mu_i\,\mu_j\,\overset{o}{a}_{ij} - \mu_i^2\,\overset{o}{a}_{jj})\Bigg]\Bigg\}. \end{aligned} \tag{2.23}$$

3. *Molar constants of magnetic saturation*

Magnetic saturation in an electric field. When a diamagnetic medium is subjected to the effect of a measuring magnetic field $\boldsymbol{H}'$ and of a strong electric polarizing field $\boldsymbol{E}$, the potential energy assumed by the p-th molecule of the medium immersed in these fields is

$$\begin{aligned} u(\tau, \boldsymbol{H}', \boldsymbol{E})^{(p)} = u(\tau)^{(p)} - \left(\mu_i^{(p)}\,F^{(p)}_{ei} + \frac{1}{2}\,a^{e(p)}_{ij}\,F^{(p)}_{ei}\,F^{(p)}_{ej} + \ldots\right) - \\ - \frac{1}{2}\left(a^{m(p)}_{ij} + b^{me(p)}_{ij,k}\,F^{(p)}_{ek} + \frac{1}{2}\,c^{me(p)}_{ij,kl}\,F^{(p)}_{ek}\,F^{(p)}_{el} + \ldots\right)F'^{(p)}_{mi}\,F'^{(p)}_{mj} - \ldots \end{aligned} \tag{3.1}$$

wherein $b^{me(p)}_{ij,k}$ and $c^{me(p)}_{ij,kl}$ are the tensors of the electro-magnetic deformability of the p-th molecule, and $F'^{(p)}_{mi}$ denotes the magnetic local measuring field acting upon the p-th molecule of the medium. The tensor $b^{me(p)}_{ij,k}$ is symmetrical in the indices i, j, and $c^{me(p)}_{ij,kl}$ — in the pairs of indices i, j and k, l.

By (3.1), the magnetic moment of the p-th molecule of the diamagnetic medium is

$$m_i^m(\tau, \boldsymbol{H}', \boldsymbol{E})^{(p)} = \left(a_{ij}^{m(p)} + b_{ij,k}^{me(p)} F_{ek}^{(p)} + \right.$$
$$\left. + \frac{1}{2} c_{ij,kl}^{me(p)} F_{ek}^{(p)} F_{el}^{(p)} + \ldots \right) F_{mj}'^{(p)} + \ldots . \tag{3.2}$$

By eqs. (3.1) and (3.2) (see Appendix), for a diamagnetic liquid, the molar constant of magnetic saturation in an electric field is

$$S_M^{me} = \frac{2\pi N_A}{135} \left\{ 5 \left(c_{ii,jj}^{me} + \frac{2b_{ij,k}^{me} \mu_l}{kT} \left\langle \sum_q \delta_{ij} \, \omega_{kl}^{(pq)} \right\rangle \right) + \right.$$
$$+ (3 \cos^2 \Omega_{me} - 1) \left[3c_{ij,ij}^{me} - c_{ii,jj}^{me} + \frac{2b_{ij,k}^{me} \mu_l}{kT} \left\langle \sum_q (3\delta_{ik} \, \omega_{jl}^{(pq)} - \delta_{ij} \, \omega_{kl}^{(pq)} \right\rangle + \right.$$
$$+ \frac{a_{ij}^m a_{kl}^e}{kT} \left\langle \sum_q (3\omega_{ik}^{(pq)} \, \omega_{jl}^{(pq)} - \delta_{ij} \, \delta_{kl}) \right\rangle +$$
$$\left.\left. + \frac{a_{ij}^m \mu_k \mu_l}{k^2 T^2} \left\langle \sum_{qr} (3\omega_{ik}^{(pq)} \, \omega_{jl}^{(pr)} - \delta_{ij} \, \omega_{kl}^{(qr)}) \right\rangle \right] \right\}, \tag{3.3}$$

with Ω_{me} denoting the angle subtended by the vectors $\boldsymbol{H}'$ and $\boldsymbol{E}$.

For a diamagnetic gas, eq. (3.3) reduces to

$${}_{\mathrm{gas}}S_M^{me} = \frac{2\pi N_A}{135} \left\{ 5 \left(c_{ii,jj}^{me} + \frac{2}{kT} \, b_{ii,j}^{me} \, \mu_i \right) + \right.$$
$$+ (3 \cos^2 \Omega_{me} - 1) \left[3c_{ij,ij}^{me} - c_{ii,jj}^{me} + \frac{2}{kT} (3b_{ij,i}^{me} \, \mu_j - b_{ii,j}^{me} \, \mu_j) + \right.$$
$$\left.\left. + \frac{1}{kT} (3a_{ij}^m a_{ij}^e - a_{ii}^m a_{jj}^e) + \frac{1}{k^2 T^2} (3a_{ij}^m \, \mu_i \, \mu_j - a_{ii}^m \, \mu_j^2) \right] \right\}. \tag{3.4}$$

Magnetic saturation in a magnetic field. By analogy, for a diamagnetic liquid, the molar constant of magnetic saturation in a magnetic field is obtained in the form

$$S_M^{mm} = \frac{2\pi N_A}{135} (1 + 2 \cos^2 \Omega_{mm}) \left\{ 3c_{iijj}^{mm} + \right.$$
$$\left. + \frac{2a_{ij}^m a_{kl}^m}{kT} \left\langle \sum_q (3\omega_{ik}^{(pq)} \, \omega_{jl}^{(pq)} - \delta_{ij} \, \delta_{kl}) \right\rangle \right\}, \tag{3.5}$$

wherein c_{ijkl}^{mm} is the tensor, symmetrical in all indices i, j, k, l, of the magneto-magnetic deformability of the molecule, and Ω_{mm} is the angle subtended by the vectors $\boldsymbol{H}'$ and $\boldsymbol{H}$.

For a diamagnetic gas, eq. (3.5) reduces to

$${}_{\mathrm{gas}}S_M^{mm} = \frac{2\pi N_A}{135} (1 + 2 \cos^2 \Omega_{mm}) \left\{ 3c_{iijj}^{mm} + \frac{2}{kT} (3a_{ij}^m \, a_{ij}^m - a_{ii}^m \, a_{jj}^m) \right\}. \tag{3.6}$$

Magnetic saturation in an optical field. Similarly, the molar constant of magnetic saturation in an optical field, for a diamagnetic liquid, is obtained in the form

$$S_M^{mo} = \frac{2\pi N_A}{135} \Big\{ 5c^{mo}_{ii,jj} + (3\cos^2 \Omega_{mo} - 1) \Big[3c^{mo}_{ij,ij} - c^{mo}_{ii,jj} + \\ + \frac{\overset{m}{a}_{ij} \overset{o}{a}_{kl}}{kT} \Big\langle \sum_q (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij}\delta_{kl}) \Big\rangle \Big] \Big\}, \tag{3.7}$$

wherein $c^{mo}_{ij,kl}$ is the tensor symmetrical in the pairs of indices i, j and k, l, of the optico-magnetic deformability of the molecule, and Ω_{mo} is the angle subtended by the vectors $\boldsymbol{H}'$ and $\mathcal{E}$.

For a diamagnetic gas, eq. (3.7) reduces to

$${}_{\text{gas}}S_M^{mo} = \frac{2\pi N_A}{135} \Big\{ 5c^{mo}_{ii,jj} + (3\cos^2 \Omega_{mo} - 1) \Big[3c^{mo}_{ij,ij} - c^{mo}_{ii,jj} + \\ + \frac{1}{kT} (3\overset{m}{a}_{ij} \overset{o}{a}_{ij} - \overset{m}{a}_{ii} \overset{o}{a}_{jj}) \Big] \Big\}. \tag{3.8}$$

4. *Molar constants of optical saturation*

Optical saturation in an electric field. Assume the medium immersed in a constant polarizing electric field $\boldsymbol{E}$ is illuminated by a light beam whose rapidly varying electric field is the measuring field $\mathcal{E}'$. The vectors $\boldsymbol{E}$ and $\mathcal{E}'$ subtend the angle Ω_{oe}.

In the presence of the fields $\mathcal{E}'$ and $\boldsymbol{E}$, the potential energy of the p-th molecule of the medium is

$$u(\tau, \mathcal{E}'. \boldsymbol{E})^{(p)} = u(\tau)^{(p)} - \left(\mu_i^{(p)} F_{ei}^{(p)} + \frac{1}{2} a_{ij}^{e(p)} F_{ei}^{(p)} F_{ej}^{(p)} + \dots \right) - \\ - \frac{1}{2} \left(a_{ij}^{o(p)} + b_{ij,k}^{oe(p)} F_{ek}^{(p)} + \frac{1}{2} c_{ij,kl}^{oe(p)} F_{ek}^{(p)} F_{el}^{(p)} + \dots \right) F_{oi}^{\prime(p)} F_{oj}^{\prime(p)} + \dots, \tag{4.1}$$

wherein $b_{ij,k}^{oe(p)}$ and $c_{ij,kl}^{oe(p)}$ are the tensors of the electro-optical deformability of the p-th molecule (the former being symmetrical in the indices i, j, and the latter in the pairs of indices i, j and k, l), and $F_{oi}^{\prime(p)}$ is the local optical measuring field acting upon the p-th molecule of the medium.

The tensor of the optical polarizability of the p-th molecule in the presence of the fields $\mathcal{E}'$ and $\boldsymbol{E}$ is

$$\alpha_{ij}^{o(p)}(\tau, \boldsymbol{E}) \equiv - \frac{d^2 u(\tau, \mathcal{E}', \boldsymbol{E})^{(p)}}{dF_{oi}^{\prime(p)} \, dF_{oj}^{\prime(p)}} . \tag{4.2}$$

By (4.1), this yields

$$\alpha_{ij}^{o(p)}(\tau, \boldsymbol{E}) = a_{ij}^{o(p)} + b_{ij,k}^{oe(p)} F_{ek}^{(p)} + \frac{1}{2} c_{ij,kl}^{oe(p)} F_{ek}^{(p)} F_{el}^{(p)} + \dots, \tag{4.3}$$

wherein $a_{ij}^{o(p)}$ is the tensor of the optical polarizability of the p-th molecule in the absence of the electric polarizing field $\boldsymbol{E}$, and the tensors $b_{ij,k}^{oe(p)}$ and $c_{ij,kl}^{oe(p)}$ determine the direct effect of the polarizing field $\boldsymbol{E}$ on the optical polarizability of the molecule.

The mean statistical value of the optical polarizability of the molecule in the presence of the electric polarizing field $\boldsymbol{E}$ is defined as follows:

$$\langle\alpha^0\rangle_E = \frac{\int\int\ldots\int \alpha_{ij}^{o(p)}(\tau, \boldsymbol{E})\,\gamma_i^{(p)}\gamma_j^{(p)}\, e^{-\frac{\sum\limits_{p=1}^{N} u(\tau,\boldsymbol{E})^{(p)}}{kT}}\, d\tau_1\, d\tau_2 \ldots d\tau_N}{\int\int\ldots\int e^{-\frac{\sum\limits_{p=1}^{N} u(\tau,\boldsymbol{E})^{(p)}}{kT}}\, d\tau_1\, d\tau_2 \ldots d\tau_N} \tag{4.4}$$

here, the $\gamma_i^{(p)}$ are the directional cosines of the angles subtended by the axes of the molecular system of reference attached to the p-th molecule of the medium and the direction of the optical measuring field $\mathscr{E}'$, and $u\,(\tau, \boldsymbol{E})^{(p\cdot}$ denotes the part of the potential energy (4.1) of the p-th molecule dependent only on the electric polarizing field $\boldsymbol{E}$.

By (4.4), and applying the method explained in the Appendix

$$\begin{aligned}\langle\alpha^0\rangle_E = \frac{1}{3}\, a_{ii}^{o} + \frac{1}{90}\Bigg\{&3\,(2 - \cos^2\Omega_{oe})\left(c_{ii,jj}^{oe} + \frac{2b_{ij,k}^{oe}\mu_l}{kT}\left\langle\sum_q \delta_{ij}\,\omega_{kl}^{(pq)}\right\rangle\right) + \\ &+ (3\cos^2\Omega_{oe} - 1)\Bigg[3c_{ij,ij}^{oe} + \frac{6b_{ij,k}^{oe}\,\mu_l}{kT}\left\langle\sum_q \delta_{ik}\,\omega_{jl}^{(pq)}\right\rangle + \\ &+ \frac{a_{ij}^{o}\,a_{kl}^{e}}{kT}\left\langle\sum_q (3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\delta_{kl})\right\rangle + \\ &+ \frac{a_{ij}^{o}\,\mu_k\,\mu_l}{k^2\,T^2}\left\langle\sum_{qr} (3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\omega_{kl}^{(qr)})\right\rangle\Bigg]\Bigg\}\, F_e^2 + \ldots\end{aligned} \tag{4.5}$$

The molar constant of the optical saturation in an electric field is defined as follows:

$$S_M^{oe} \equiv \frac{4\pi}{3}\,\frac{N_A}{F_e^2}\,(\langle\alpha^o\rangle_E - \langle\alpha^o\rangle_{E=0}), \tag{4.6}$$

yielding, by (4.5), for polar liquids

$$\begin{aligned}S_M^{oe} = \frac{2\pi\,N_A}{135}\Bigg\{&5\left(c_{ii,jj}^{oe} + \frac{2b_{ij,k}^{oe}\,\mu_l}{kT}\left\langle\sum_q \delta_{ij}\,\omega_{kl}^{(pq)}\right\rangle\right) + \\ &+ (3\cos^2\Omega_{oe} - 1)\Bigg[3c_{ij,ij}^{oe} - c_{ii,jj}^{oe} + \frac{2b_{ij,k}^{oe}\,\mu_j}{kT}\left\langle\sum_q (3\delta_{ik}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\omega_{kl}^{(pq)})\right\rangle +\end{aligned}$$

$$+\frac{a^{o}_{ij}\,a^{e}_{kl}}{kT}\left\langle\sum_{q}\left(3\omega^{(pq)}_{ik}\,\omega^{(pq)}_{jl}-\delta_{ij}\,\delta_{kl}\right)\right\rangle+$$

$$+\frac{a^{o}_{ij}\,\mu_k\,\mu_l}{k^2\,T^2}\left\langle\sum_{qr}\left(3\omega^{(pq)}_{ik}\,\omega^{(pr)}_{jl}-\delta_{ij}\,\omega^{(qr)}_{kl}\right)\right\rangle\Bigg]\Bigg\}, \tag{4.7}$$

and, for a polar gas,

$$_{\mathrm{gas}}S^{oe}_{M}=\frac{2\pi\,N_A}{135}\Bigg\{5\left(c^{oe}_{ii,jj}+\frac{2}{kT}\,b^{oe}_{ii,j}\,\mu_j\right)+$$

$$+\left(3\cos^2\Omega_{oe}-1\right)\Bigg[3c^{oe}_{ij,ij}-c^{oe}_{ii,jj}+\frac{2}{kT}\left(3b^{oe}_{ij,i}\,\mu_j-b^{oe}_{ii,j}\,\mu_j\right)+$$

$$+\frac{1}{kT}\left(3a^{o}_{ij}\,a^{e}_{ij}-a^{o}_{ii}\,a^{e}_{jj}\right)+\frac{1}{k^2\,T^2}\left(3a^{o}_{ij}\,\mu_i\,\mu_j-a^{o}_{ii}\,\mu^2_j\right)\Bigg]\Bigg\}. \tag{4.8}$$

Optical saturation in a magnetic field. By analogy, the molar constant of the optical saturation in a magnetic field (magneto-optical saturation) is obtained for a diamagnetic liquid:

$$S^{om}_{M}=\frac{2\pi\,N_A}{135}\Bigg\{5c^{om}_{ii,jj}+\left(3\cos^2\Omega_{om}-1\right)\Bigg[3c^{om}_{ij,ij}-c^{om}_{ii,jj}+$$

$$+\frac{a^{o}_{ij}\,a^{m}_{kl}}{kT}\left\langle\sum_{q}\left(3\omega^{(pq)}_{ik}\,\omega^{(pq)}_{jl}-\delta_{ij}\,\delta_{kl}\right)\right\rangle\Bigg]\Bigg\}, \tag{4.9}$$

wherein $c^{om}_{ij,kl}$ is the tensor symmetrical in the pairs of indices i, j and k, l, of the magneto-optical saturation, and Ω_{om} denotes the angle subtended by the vectors $\mathcal{E}'$ and $\boldsymbol{H}$.

For a diamagnetic gas, the foregoing equation reduces to

$$_{\mathrm{gas}}S^{om}_{M}=\frac{2\pi\,N_A}{135}\Bigg\{5c^{om}_{ii,jj}+\left(3\cos^2\Omega_{om}-1\right)\Bigg[3c^{om}_{ij,ij}-c^{om}_{ii,jj}+$$

$$+\frac{1}{kT}\left(3a^{o}_{ij}\,a^{m}_{ij}-a^{o}_{ii}\,a^{m}_{jj}\right)\Bigg]\Bigg\}. \tag{4.10}$$

Optical saturation in an optical field. Finally, the case will be considered when not only the measuring field $\mathcal{E}'$, but the polarizing field $\mathcal{E}=\mathcal{E}_a\cos 2\,\pi\,\nu\,t$, too, is an optical field. By averageing the rapidly variable polarizing field, eqs. (4.1) and (4.3) now yield

$$\widetilde{u\left(\tau,\mathcal{E}\right)^{(p)}}=u\left(\tau\right)^{(p)}-\frac{1}{2}\,a^{o(p)}_{ij}\,\widetilde{F^{(p)}_{oi}\,F^{(p)}_{oj}}-\ldots, \tag{4.11}$$

and

$$\widetilde{\alpha^{o'}_{ij}\left(\tau,\mathcal{E}\right)^{(p)}}=a^{o'(p)}_{ij}+\frac{1}{2}\,c^{o'o(p)}_{ij,kl}\,\widetilde{F^{(p)}_{ok}\,F^{(p)}_{ol}}+\ldots, \tag{4.12}$$

wherein $a_{ij}^{o(p)}$ and $a_{ij}^{o'(p)}$ denote the tensors of the optical polarizability of the molecule as relating to the optical polarizing and measuring fields, respectively, and $c_{ij,kl}^{o'o(p)}$ — the tensor of the optico-optical deformability of the p-th molecule of the medium; the latter is, in general, symmetrical in the first and second pair of indices separately.

By the method discussed in the Appendix, eqs. (4.11) and (4.12) yield the mean statistical value of the optical polarizability of the molecule in the presence of the optical polarizing field:

$$\langle \alpha^0 \rangle_{\mathcal{E}} = \frac{1}{3} a_{ii}^{o'} + \frac{1}{90} \Big\{ 3\,(2 - \cos^2 \Omega_{oo}')\, c_{ii,jj}^{o'o} + \\ + (3\cos^2 \Omega_{oo} - 1) \Big[3 c_{ij,ij}^{o'o} + \frac{a_{ij}^{o'} a_{kl}^{o}}{kT} \Big\langle \sum_q (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij}\delta_{kl}) \Big\rangle \Big] \Big\} \widetilde{F_o^2}, \tag{4.13}$$

wherein Ω_{oo} denotes the angle subtended by the vectors $\mathcal{E}'$ and $\mathcal{E}$.

By (4.13), the molar constant of the optical saturation in an optical field, defined in analogy to (4.6) is, for a liquid

$$S_M^{oo} = \frac{2\pi N_A}{135} \Big\{ 5 c_{ii,jj}^{o'o} + (3\cos^2 \Omega_{oo} - 1) \Big[3 c_{ij,ij}^{o'o} - c_{ii,jj}^{o'o} + \\ + \frac{a_{ij}^{o'} a_{kl}^{o}}{kT} \Big\langle \sum_q (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij}\delta_{kl}) \Big\rangle \Big] \Big\}, \tag{4.14}$$

and, for a gas

$${}_{\text{gas}}S_M^{oo} = \frac{2\pi N_A}{135} \Big\{ 5 c_{ii,jj}^{o'o} + (3\cos^2 \Omega_{oo} - 1) \Big[3 c_{ij,ij}^{o'o} - c_{ii,jj}^{o'o} + \\ + \frac{1}{kT} (3 a_{ij}^{o'} a_{ij}^{o} - a_{ii}^{o'} a_{jj}^{o}) \Big] \Big\}. \tag{4.15}$$

If the frequency of the measuring field vector $\mathcal{E}'$ and that of the polarizing field vector $\mathcal{E}$ are equal or differ but insignificantly, then $a_{ij}^{o'} = a_{ij}^{o}$ and $c_{ij,kl}^{o'o} = c_{ijkl}^{oo}$, the tensor c_{ijkl}^{oo} being symmetrical in all the indices, and eqs. (4.14) may be written in the form

$$S_M^{oo} = \frac{2\pi N_A}{135} \Big\{ 3\,(1 + 2\cos^2 \Omega_{oo})\, c_{iijj}^{oo} + \\ + (3\cos^2 \Omega_{oo} - 1) \frac{a_{ij}^{o} a_{kl}^{o}}{kT} \Big\langle \sum_q (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij}\delta_{kl}) \Big\rangle \Big\}, \tag{4.16}$$

and

$${}_{\text{gas}}S_M^{oo} = \frac{2\pi N_A}{135} \Big\{ 3\,(1 + 2\cos^2 \Omega_{oo})\, c_{iijj}^{oo} + \frac{1}{kT} (3\cos^2 \Omega_{oo} - 1)\, (3 a_{ij}^{o} a_{ij}^{o} - a_{ii}^{o} a_{jj}^{o}) \Big\}. \tag{4.17}$$

Optical birefringence in an electric, magnetic or optical field. It is the molar constants of the optical birefringence that are usually computed in optical phenomena, as the molar constants of the optical saturation determine the absolute value of the effect arising in anisotropic medium subjected to a polarizing field ("retard absolu") Thus, e. g., the molar constant of the optical birefringence in an electric field, or the so-called molar Kerr constant, is defined as

$$B_M^{oe} \equiv \frac{4\pi}{3}\frac{N_A}{F_e^2}\{\langle\alpha^o\rangle_{E,\Omega_{oe}=0^\circ} - \langle\alpha^o\rangle_{E,\Omega_{oe}=90^\circ}\}. \tag{4.18}$$

or, by definition (4.6)

$$B_M^{oe} = S_{M,\Omega_{oe}=0^\circ}^{oe} - S_{M,\Omega_{oe}=90^\circ}^{oe}, \tag{4.19}$$

wherein $\langle\alpha^\circ\rangle_{E,\Omega_{oe}=0^\circ}$ and $S_{M,\Omega_{oe}=0^\circ}^{oe}$ are the values of (4.5) and (4.7) for $\Omega_{oe} = 0^\circ$ i. e. when the vectors $\mathcal{E}'$ and $\boldsymbol{E}$ are parallel, while $\langle\alpha^\circ\rangle_{E,\Omega_{oe}=90^\circ}$ and $S_{M,\Omega_{oe}=90^\circ}^{oe}$ represent the respective values for $\Omega_{eo} = 90^\circ$, i. e. when the vectors $\mathcal{E}'$ and $\boldsymbol{E}$ are perpendicular.

The remaining molar constants of the optical birefringence are defined similarly: B_M^{om} is the molar constant of the optical birefringence in a magnetic field, or Cotton-Mouton's molar constant, and B_M^{oo} is that of the optical birefringence in an optical field, or Buckingham's molar constant (in the paper by Buckingham, the constant B_M^{oo} is defined differently and hence differs by a factor of $^1/_9$, see Buckingham 1956 b).

By the foregoing definitions, eqs. (4.7), (4.9) and (4.14) yield for condensed media

$$\begin{aligned} B_M^{oe} = \frac{2\pi N_A}{45}\Bigg\{&3c_{ij,ij}^{oe} - c_{ii,jj}^{oe} + \frac{2b_{ij,k}^{oe}\,\mu_l}{kT}\left\langle\sum_q (3\delta_{ik}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\omega_{kl}^{(pq)})\right\rangle + \\ &+ \frac{\overset{o}{a}_{ij}\,\overset{e}{a}_{kl}}{kT}\left\langle\sum_q (3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\delta_{kl})\right\rangle + \\ &+ \frac{\overset{o}{a}_{ij}\,\mu_k\,\mu_l}{k^2\,T^2}\left\langle\sum_{qr} (3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pr)} - \delta_{ij}\,\omega_{kl}^{(qr)})\right\rangle\Bigg\}, \end{aligned} \tag{4.20}$$

$$B_M^{om} = \frac{2\pi N_A}{45}\left\{3c_{ij,ij}^{om} - c_{ii,jj}^{om} + \frac{\overset{o}{a}_{ij}\,\overset{m}{a}_{kl}}{kT}\left\langle\sum_q (3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\delta_{kl})\right\rangle\right\}, \tag{4.21}$$

$$B_M^{oo} = \frac{2\pi N_A}{45}\left\{3c_{ij,ij}^{o'o} - c_{ij,ij}^{o'o} + \frac{\overset{o'}{a}_{ij}\,\overset{o}{a}_{kl}}{kT}\left\langle\sum_q (3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\delta_{kl})\right\rangle\right\}. \tag{4.22}$$

For a gaseous medium, the molar constants of the optical birefringence reduce to

$$\begin{aligned} {}_{\text{gas}}B_M^{oe} = \frac{2\pi N_A}{45}\Bigg\{&3c_{ij,ij}^{oe} - c_{ii,jj}^{oe} + \frac{2}{kT}(3b_{ij,i}^{oe}\,\mu_j - b_{ii,j}^{oe}\,\mu_j) + \\ &+ \frac{1}{kT}(3\overset{o}{a}_{ij}\overset{e}{a}_{ij} - \overset{o}{a}_{ii}\,\overset{e}{a}_{jj}) + \frac{1}{k^2\,T^2}(3\overset{o}{a}_{ij}\,\mu_i\,\mu_j - \overset{o}{a}_{ii}\,\mu_j^2)\Bigg\}, \end{aligned} \tag{4.23}$$

$${}_{\text{gas}}B_M^{om} = \frac{2\pi N_A}{45}\left\{3c^{om}_{ij,ij} - c^{om}_{ii,jj} + \frac{1}{kT}\left(3a^{o}_{ij}a^{m}_{ij} - a^{o}_{ii}a^{m}_{jj}\right)\right\}, \tag{4.24}$$

$${}_{\text{gas}}B_M^{oo} = \frac{2\pi N_A}{45}\left\{3c^{o'o}_{ij,ij} - c^{o'o}_{ii,jj} + \frac{1}{kT}\left(3a^{o'}_{ij}a^{o}_{ij} - a^{o'}_{ii}a^{o}_{jj}\right)\right\}. \tag{4.25}$$

Kerr's molar constant given for a gas by eq. (4.23) consists, in general, of four terms. The first of these, $3\,c^{oe}_{ii,ij} - c^{oe}_{ii,jj}$, accounts for Voigt's purely deformational effect (1901; 1908), and is temperature - independent. As proved by Langevin (1910), this effect is extremely insignificant in most substances, as compared with the remaining terms. It is of account in monatomic gases and in substances whose molecules possess the spherical symmetry (see Buckingham and Pople, 1955, 1956). The term $2(3\,b^{oe}_{ij,i}\,\mu_j - b_{ii,j}\,\mu_j)(kT)^{-1}$ accounts for Born's deformational-orientational effect (1933). The remaining two, namely, the purely anisotropic term $(3\,a^o_{ij}\,a^e_{ij} - a^o_{ii}\,a^e_{jj})(kT)^{-1}$ and the anisotropic-dipolar term $(3\,a^o_{ij}\,\mu_i\,\mu_j - a^o_{ii}\,\mu_j^2)(kT)^{-2}$, account for the Langevin-Born effect of molecular orientation. In liquids (eq. (4.20)), the latter two, i. e. the deformational-orientational and purely orientational effects are influenced by molecular interaction. The term $3\,c^{om}_{ij,ij} - c^{om}_{ii,jj}$ in the Cotton-Mouton molar constant accounts for Voigt's deformational effect, whereas the term $(3\,a^o_{ij}\,a^m_{ij} - a^o_{ii}\,a^m_{jj})(kT)^{-1}$ determines Langevin's orientational effect (1910). It will be seen by (4.21) that, in liquids, this latter effect is intimately connected with molecular interaction. The presence in eq. (4.25) of the anisotropic term $(3\,a^{o'}_{ij}\,a^o_{ij} - a^{o'}_{ii}\,a^o_{jj})\,(kT)^{-1}$ points to the fact that the polarizing optical field also tends to order the anisotropic molecules, thus causing the isotropic medium to become optically anisotropic, with its optical axis parallel to the oscillating electric vector of the optical polarizing field. In a condensed medium, by eq. (4.22), this effect of molecular orientation is modified by molecular interaction. Moreover, by eqs. (4.22) and (4.25) it will be seen that in the present case, too, there is a purely deformational effect described by the term $3\,c^{o'o}_{ij,ij} - c^{o'o}_{ii,jj}$, an effect that is independent of the temperature and of molecular interaction (see Buckingham, 1956 b).

5. *The molar constant of the nine effects of saturation, computed for some special cases*

In §§ 2, 3 and 4, general expressions for the molar constants of the nine saturation effects originally enumerated have been derived without any assumptions whatsoever as to the symmetry of the molecules and the nature of the intermolecular forces. Now some special cases will be considered.

Spherical molecules. If the molecules of an isotropic medium possess the spherical symmetry, the tensors of odd order vanish:

$$\mu_i = 0,\ b^{ee}_{ijk} = b^{oe}_{ij,k} = \ldots = 0$$

whereas those of even order reduce to isotropic tensors given by the following relationships:

$$a_{ij} = a\,\delta_{ij},$$

$$c_{ijkl} = \frac{1}{3}\,c\,(\delta_{ij}\,\delta_{kl} + \delta_{ik}\,\delta_{jl} + \delta_{il}\,\delta_{kj}),$$

$$c_{ij,kl} = x\,\delta_{ij}\,\delta_{kl} + y\,(\delta_{ik}\,\delta_{jl} + \delta_{il}\,\delta_{kj}). \tag{5.1}$$

To simplify notation, the non-vanishing components of the last tensor, which is isotropic of order 4, will be written as follows (see Buckingham and Pople, 1956):

$$c_{ij,kl} = x + 2y = c_{||}\,, \quad \text{for } i = j = k = l,$$

$$c_{ij,kl} = x = c_{\perp}\,, \quad \text{for } i = j,\ k = l,$$

$$c_{ij,kl} = y = \frac{1}{2}\,(c_{||} - c_{\perp}), \quad \text{for } i = k, \quad j = l. \tag{5.2}$$

All tensors, a_{ij}, c_{ijkl} and $c_{ij,kl}$, as well as the corresponding scalar values a, c, $c_{||}$ and $c_{\perp}$ should be provided with upper indices explaining the nature of the measuring and polarizing fields, respectively, e. g. a^{e}_{ij}, a^{e}, $c^{em}_{ij,kl}$, $c^{em}_{||}$, $c^{em}_{\perp}$, etc. The scalar coefficients $c_{||}$ and $c_{\perp}$ (with suitable upper indices) denote the electric, magnetic or optical deformability of the molecule in the direction parallel or perpendicular to that of the polarizing field, the nature of which is made apparent by the second upper index.

By (5.1) and (5.2), the general expressions derived in §§ 2, 3 and 4 giving the nine molar constants of saturation assume the following form valid both for gaseous and liquid media:

$$S^{ee}_{M} = \frac{2\pi N_A}{9}\,(1 + 2\cos^2 \Omega_{ee})\,c^{ee},$$

$$S^{em}_{M} = \frac{2\pi N_A}{9}\,\{c^{em}_{||} + 2c^{em}_{\perp} + (3\cos^2 \Omega_{em} - 1)\,(c^{em}_{||} - c^{em}_{\perp})\}, \tag{5.3}$$

$$S^{eo}_{M} = \frac{2\pi N_A}{9}\,\{c^{eo}_{||} + 2c^{eo}_{\perp} + (3\cos^2 \Omega_{eo} - 1)\,(c^{eo}_{||} - c^{eo}_{\perp})\},$$

$$S^{me}_{M} = \frac{2\pi N_A}{9}\,\{c^{me}_{||} + 2c^{me}_{\perp} + (3\cos^2 \Omega_{me} - 1)\,(c^{me}_{||} - c^{me}_{\perp})\},$$

$$S^{mm}_{M} = \frac{2\pi N_A}{9}\,(1 + 2\cos^2 \Omega_{mm})\,c^{mm},$$

$$S^{mo}_{M} = \frac{2\pi N_A}{9}\,\{c^{mo}_{||} + 2c^{mo}_{\perp} + (3\cos^2 \Omega_{mo} - 1)\,(c^{mo}_{||} - c^{mo}_{\perp})\}, \tag{5.4}$$

$$S^{oe}_{M} = \frac{2\pi N_A}{9}\,\{c^{oe}_{||} + 2c^{oe}_{\perp} + (3\cos^2 \Omega_{oe} - 1)\,(c^{oe}_{||} - c^{oe}_{\perp})\},$$

$$S_M^{oo} = \frac{2\pi N_A}{9} \{c_{\|}^{om} + 2c_{\perp}^{om} + (3\cos^2 \Omega_{om} - 1)(c_{\|}^{om} - c_{\perp}^{om})\},$$

$$S_M^{om} = \frac{2\pi N_N}{9} (1 + 2\cos^2 \Omega_{oo}) c^{oo}. \tag{5.5}$$

The foregoing molar constants of saturation contain *only* deformational terms independent of the temperature and of molecular interaction. This is indicative of the fact that in an isotropic medium composed of spherical molecules the saturation arises solely and exclusively from nonlinear deformation produced in the molecule through the direct agency of the strong external polarizing field.

In the present case, the molar constants of the optical birefringences (4.20) — — (4.22), by (5.1) and (5.2) assume the form

$$B_M^{oe} = \frac{2\pi N_A}{3} (c_{\|}^{oe} - c_{\perp}^{oe}),$$

$$B_M^{om} = \frac{2\pi N_A}{3} (c_{\|}^{om} - c_{\perp}^{om}),$$

$$B_M^{oo} = \frac{2\pi N_A}{3} (c_{\|}^{o'o} - c_{\perp}^{o'o}). \tag{5.6}$$

Thus, an isotropic medium becomes optically birefringent although its molecules are spherically symmetric. In this case, the medium exhibits anisotropy only because the strong external polarizing field induces the anisotropy directly in the molecule. This is precisely Voigt's deformational effect (1901, 1908), which, it will be remembered, is extremely small as compared with the orientational effect existing when the molecules are anisotropic or polar anisotropic.

Polar-anisotropic molecules. For strongly polar anisotropic molecules, the small deformational effect may be neglected, i. e. the problem reduces to the effect of pure molecular orientation which now is the only one to play an important part. The nine molar constants derived in §§ 2, 3 and 4 now reduce to the following six:

$$\begin{aligned} S_M^{ee} = \frac{2\pi N_A}{135} (1 + 2\cos^2 \Omega_{ee}) \Bigg\{ & \frac{2a_{ij}^e a_{kl}^e}{kT} \Big\langle \sum_q (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij}\delta_{kl}) \Big\rangle + \\ & + \frac{4a_{ij}^e \mu_k \mu_l}{k^2T^2} \Big\langle \sum_{qr} (3\omega_{ik}^{(pq)} \omega_{jl}^{(pr)} - \delta_{ij}\omega_{kl}^{(qr)}) \Big\rangle + \\ & + \frac{\mu_i \mu_j \mu_k \mu_l}{k^3T^3} \left(3 \Big\langle \sum_{qrs} \omega_{ij}^{(pq)} \omega_{kl}^{(rs)} \Big\rangle - 5 \Big\langle \sum_q \omega_{ij}^{(pq)} \Big\rangle \Big\langle \sum_{rs} \omega_{kl}^{(rs)} \Big\rangle \right) \Bigg\}, \end{aligned} \tag{5.7}$$

$$\begin{aligned} S_M^{em} = S_M^{me} = \frac{2\pi N_A}{135} (3\cos^2 \Omega_{em} - 1) \Bigg\{ & \frac{a_{ij}^e a_{kl}^m}{kT} \Big\langle \sum_q (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij}\delta_{kl}) \Big\rangle + \\ & + \frac{a_{ij}^m \mu_k \mu_l}{k^2T^2} \Big\langle \sum_{qr} (3\omega_{ik}^{(pq)} \omega_{jl}^{(pr)} - \delta_{ij}\omega_{kl}^{(qr)}) \Big\rangle \Bigg\}, \end{aligned} \tag{5.8}$$

$$S_M^{eo} = S_M^{eo} = \frac{2\pi N_A}{135}(3\cos^2\Omega_{eo} - 1)\left\{\frac{a_{ij}^{e}\,a_{kl}^{o}}{kT}\left\langle\sum_{q}(3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\delta_{kl})\right\rangle + \right.$$
$$\left. + \frac{a_{ij}^{o}\,\mu_k\,\mu_l}{k^2T^2}\left\langle\sum_{qr}(3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pr)} - \delta_{ij}\,\omega_{kl}^{(qr)})\right\rangle\right\}, \tag{5.9}$$

$$S_M^{mm} = \frac{4\pi N_A}{135}(1 + 2\cos^2\Omega_{mm})\,\frac{a_{ij}^{m}\,a_{kl}^{m}}{kT}\left\langle\sum_{q}(3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\delta_{kl})\right\rangle, \tag{5.10}$$

$$S_M^{mo} = S_M^{om} = \frac{2\pi N_A}{135}(3\cos^2\Omega_{mo} - 1)\,\frac{a_{ij}^{m}\,a_{kl}^{o}}{kT}\left\langle\sum_{q}(3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\delta_{kl})\right\rangle, \tag{5.11}$$

$$S_M^{oo} = \frac{2\pi N_A}{135}(3\cos^2\Omega_{oo} - 1)\,\frac{a_{ij}^{o}\,a_{kl}^{o}}{kT}\left\langle\sum_{q}(3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\delta_{kl})\right\rangle. \tag{5.12}$$

The foregoing molar constants, in general, account for nine effects of molecular orientation produced within the condensed medium by an electric, magnetic or optical polarizing field.

If the polar and anisotropic molecules possess the axial symmetry, and if the axis of symmetry is the 3-axis, then

$$\mu_1 = \mu_2 = 0,\ \ \mu_3 \neq 0,\quad a_{ij}^{e} = a_{ij}^{m} = a_{ij}^{o} = 0 \text{ for } i \neq j$$
$$a_{11}^{e} = a_{22}^{e} \neq a_{33}^{e},\quad a_{11}^{m} = a_{22}^{m} \neq a_{33}^{m},\quad a_{11}^{o} = a_{22}^{o} \neq a_{33}^{o}. \tag{5.13}$$

Now, by the general formula of the directional cosines of the angles between the axes of the particular molecular systems of reference:

$$\omega_{\sigma i}^{(pq)}\,\omega_{\sigma j}^{(pr)} = \begin{cases}\delta_{ij} & \text{for } q = r\\ \omega_{ij}^{(qr)} & \text{for } q \neq r,\end{cases} \tag{5.14}$$

eqs. (5.7) — (5.12) yield (see Piekara and Kielich, 1958 *c*)

$$S_M^{ee} = \frac{4\pi N_A}{135}(1 + 2\cos^2\Omega_{ee})\left(\frac{2\mathcal{H}^e\mathcal{H}^e}{kT}R_{CM} + \frac{4\mathcal{H}^e\mu_3^2}{k^2T^2}R_K - \frac{\mu_3^4}{k^3T^3}R_S\right), \tag{5.15}$$

$$S_M^{em} = S_M^{me} = \frac{4\pi N_A}{135}(3\cos^2\Omega_{em} - 1)\left(\frac{\mathcal{H}^e\mathcal{H}^m}{kT}R_{CM} + \frac{\mathcal{H}^m\mu_3^2}{k^2T^2}R_K\right), \tag{5.16}$$

$$S_M^{eo} = S_M^{oe} = \frac{4\pi N_A}{135}(3\cos^2\Omega_{eo} - 1)\left(\frac{\mathcal{H}^e\mathcal{H}^o}{kT}R_{CM} + \frac{\mathcal{H}^o\mu_3^2}{k^2T^2}R_K\right), \tag{5.17}$$

$$S_M^{mm} = \frac{8\pi N_A}{135}(1 + 2\cos^2\Omega_{mm})\,\frac{\mathcal{H}^m\mathcal{H}^m}{kT}R_{CM}, \tag{5.18}$$

$$S_M^{mo} = S_M^{om} = \frac{4\pi N_A}{135}(3\cos^2\Omega_{mo} - 1)\,\frac{\mathcal{H}^m\mathcal{H}^o}{kT}R_{CM}, \tag{5.19}$$

$$S_M^{oo} = \frac{4\pi N_A}{135}(3\cos^2\Omega_{oo} - 1)\,\frac{\mathcal{H}^o\mathcal{H}^o}{kT}R_{CM}, \tag{5.20}$$

wherein the quantities

$$\mathcal{H}^{e} = a^{e}_{33} - a^{e}_{11}, \quad \mathcal{H}^{m} = a^{m}_{33} - a^{m}_{11}, \quad \mathcal{H}^{o} = a^{o}_{33} - a^{o}_{11}, \tag{5.21}$$

are the anisotropies of the electric, magnetic and optical polarizabilities of the medium, respectively.

The quantities R_{CM}, R_K and R_S in eqs. (5.15) — (5.20) are respectively of the form

$$R_{CM} = \frac{1}{2} \left\langle \sum_{q} (3 \cos^2 \Theta^{(pq)} - 1) \right\rangle, \tag{5.22}$$

$$R_K = \frac{1}{2} \left\langle \sum_{qr} (3 \cos \Theta^{(pq)} \cos \Theta^{(pr)} - \cos \Theta^{(qr)}) \right\rangle, \tag{5.23}$$

$$R_S = \frac{1}{2} \left(5 \left\langle \sum_{q} \cos \Theta^{(pq)} \right\rangle \left\langle \sum_{rs} \cos \Theta^{(rs)} \right\rangle - 3 \left\langle \sum_{qrs} \cos \Theta^{(pq)} \cos \Theta^{(rs)} \right\rangle \right), \tag{5.24}$$

with $\theta^{(pq)}$ denoting the angle subtended by the axes of symmetry of the p-th and q-th molecules of the medium, while the mean values symbolized by the brackets $< >$ are those defined by eq. (2.9). The quantities R_{CM}, R_K and R_S account for the effect of the molecular interaction of molecules possessing the axial symmetry in a medium, and will be termed correlation factors.

Thus it results for the important case of a medium the molecules of which are axial symmetric that the effect of the molecular interaction in the nine molecular orientational effects under consideration is accounted for completely by the three correlation factors R_{CM}, R_K and R_S. This is a fact of great significance in comparing the theory proposed in the present paper with the experimental results (see the following § 6). The correlation factors R_{CM}, R_K and R_S in the form of eqs. (5.22) — (5.24) have been derived and discussed for some special models of molecular interaction in earlier papers (see Piekara and Kielich, 1957, 1958 a, 1958 b; Kielich 1958).

In particular, for the model of dipole pairwise interaction originally proposed by one of the present authors (see Piekara 1937, 1939, 1950), the correlation factors assume the form

$$R_{CM} = 2 - 3\frac{L}{y}, \quad R_K = 2 - 3\frac{L}{y} \pm 2L,$$

$$R_S = 6\frac{L}{y} - (1 \pm 5L)(1 \mp L), \tag{5.25}$$

wherein $L \equiv L(y)$ is Langevin's function, and $y = W/kT$ the potential energy of interaction of a pair of dipoles in kT units. The upper and lower signs account for the cases of a pair of dipoles tending to the parallel and antiparallel orientation, respectively.

It should be stresses that the foregoing model is in itself adequate for explaining theoretically the change in sign of the electric saturation effect produced by an external electric field in polar liquids, as experimentally observed (A. Piekara, B. Piekara, 1936). Namely, in strongly polar liquids, the purely dipolar term predominates; then, by (5.15),

$$_{\mathrm{dip}}S_M^{ee} = -\frac{4\pi N_A}{135}\left(1 + 2\cos^2\Omega_{ee}\right)\frac{\mu_3^4}{k^3 T^3} R_S . \tag{5.26}$$

If the interacting dipoles tend to the antiparallel orientation, and for the value y $\geqslant 1.33$ of the interaction energy, the correlation factor R_S changes its sign becoming negative and, hence, the molar constant of saturation (5.26) becomes positive.

If the potential energy of the molecular interaction may be neglected, $U_N = 0$, we have

$$R_{CM} = R_K = R_S = 1, \tag{5.27}$$

and eqs. (5.15) — (5.20) assume a form that holds for gaseous media.

6. *Relation between the measured variations of ε, μ and n and the molecular constants*

General relationships. By the first of eqs. (1.1) and by (2.5), the following general equation for the electric permittivity of a medium as measured by the measuring field ***E***' in the presence of a strong electric polarizing field ***E*** is obtained:

$$\varepsilon^e - 1 = 4\pi \frac{N}{V}\frac{\partial}{\partial E'}\langle m^e_{E'}\rangle_{E',E} , \tag{6.1}$$

wherein $\langle m^e_{E'}\rangle_{E',E}$ denotes the mean statistical value of the component of the electric moment of a molecule of the dielectric in the direction of the field ***E***' as defined in general by eq. (2.6) and given, on computing, by eq. (2.8).

Thus, for polar liquids, eqs. (6.1) and (2.8) yield

$$\begin{aligned}\varepsilon^e - 1 = 4\pi \frac{N}{V}\frac{\partial F'_e}{\partial E'}\Bigg\{ & a^e + \frac{\mu_i \mu_j}{3\,kT}\Big\langle \sum_q \omega_{ij}^{(pq)} \Big\rangle + \\ & + \frac{1 + 2\cos^2\Omega_{ee}}{90}\Bigg[3c^{ee}_{iijj} + \frac{12\mu_i\, b^{ee}_{jkl}}{kT}\Big\langle \sum_q \omega_{ij}^{(pq)}\,\delta_{kl}\Big\rangle + \\ & + \frac{2a^e_{ij}\, a^e_{kl}}{kT}\Big\langle \sum_q \left(3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pq)} - \delta_{ij}\,\delta_{kl}\right)\Big\rangle + \\ & + \frac{4a^e_{ij}\,\mu_k\,\mu_l}{k^2 T^2}\Big\langle \sum_{qr}\left(3\omega_{ik}^{(pq)}\,\omega_{jl}^{(pr)} - \delta_{ij}\,\omega_{kl}^{(qr)}\right)\Big\rangle + \\ & + \frac{\mu_i\,\mu_j\,\mu_k\,\mu_l}{k^3 T^3}\left(3\Big\langle\sum_{qrs}\omega_{ij}^{(pq)}\,\omega_{kl}^{(rs)}\Big\rangle - 5\Big\langle\sum_q \omega_{ij}^{(pq)}\Big\rangle\Big\langle\sum_{rs}\omega_{kl}^{(rs)}\Big\rangle\right)\Bigg] F_e^2\Bigg\};\end{aligned} \tag{6.2}$$

with $a^e = \frac{1}{3} a^e_{ii}$ denoting the mean electric polarizability of a molecule in the medium in the absence of a polarizing field.

In particular, the electric polarizability of a medium, measured in the absence of a polarizing field ($\boldsymbol{E} = 0$), is obtained in the form

$$\varepsilon - 1 = 4\pi \frac{N}{V} \left(a^e + \frac{\mu_i \mu_j}{3kT} \left\langle \sum_q \omega_{ij}^{(pq)} \right\rangle \right) \left(\frac{\partial F'_e}{\partial E'} \right)_{E=0} . \tag{6.3}$$

Eqs. (6.2) and (6.3) together yield the variation of the electric permittivity of the medium as arising from the effect of a strong electric polarizing field $\boldsymbol{E}$, i. e. $\Delta \varepsilon^e = \varepsilon^e - \varepsilon$. Restricting to small values of $\Delta \varepsilon^e$ and neglecting electrostriction and the electro-caloric effect, by eq. (2.11) the true effect of saturation is

$$\Delta \varepsilon^e_{sat} = 3 \left(1 - \frac{\partial f_e}{\partial \varepsilon^e} \right)^{-1}_{\varepsilon^e = \varepsilon} \frac{\partial F'_e}{\partial E'} \frac{S^{ee}_M}{V_M} F^2_e , \tag{6.4}$$

with

$$f_e = 4\pi \frac{N}{V} \left(a^e + \frac{\mu_i \mu_j}{3kT} \left\langle \sum_q \omega_{ij}^{(pq)} \right\rangle \right) \frac{\partial F'_e}{\partial E'} , \tag{6.5}$$

and $V_M = \dfrac{M}{\varrho}$ denoting the molar volume (M — the molecular weight and ϱ — the density of the dielectric), while S^{ee}_M is the molar constant of the electric saturation in an electric field, as given by the general eq. (2.11). Thus, a general expression relating $\Delta \varepsilon^e_{sat}$ and the molar constant S^{ee}_M in the case of electric saturation in an electric field has been derived.

The expressions relating the variations of ε, μ and n given by eqs. (1.2) — (1.4) and the respective molar constants computed in §§ 2, 3 and 4 are derived by analogy for the remaining eight effects.

In this way, neglecting the terms in the fourth and higher powers of the polarizing fields, the following set of equations accounting for all nine effects is obtained:

$$\Delta \varepsilon^e_{sat} = S^{ee} E^2, \qquad \Delta \varepsilon^m_{sat} = S^{em} H^2, \qquad \Delta \varepsilon^o_{sat} = S^{eo} \widetilde{\mathcal{E}}^2, \tag{6.6}$$

$$\Delta \mu^e_{sat} = S^{me} E^2, \qquad \Delta \mu^m_{sat} = S^{mm} H^2, \qquad \Delta \mu^o_{sat} = S^{mo} \widetilde{\mathcal{E}}^2, \tag{6.7}$$

$$\Delta (n^2)^e_{sat} = S^{oe} E^2, \qquad \Delta (n^2)^m_{sat} = S^{om} H^2, \qquad \Delta (n^2)^o_{sat} = S^{oo} \widetilde{\mathcal{E}}^2, \tag{6.8}$$

wherein specific constants of saturation S^{ee}, S^{em}, ... S^{oo} have been introduced, which are related to the molar constants S^{de}_M, ... S^{oo}_M computed in §§ 2, 3 and 4 by the following equations:

$$S^{ex} = 3\sigma^{ex} \frac{S^{ex}_M}{V_M} , \qquad S^{mx} = 3\sigma^{mx} \frac{S^{mx}_M}{V_M} , \qquad S^{ox} = 3\sigma^{ox} \frac{S^{ox}_M}{V_M} , \tag{6.9}$$

here, the place of the index x should be filled in with one of the letters e, m or o, according to the kind of polarizing field considered. The parameters σ^{ex}, σ^{mx} and σ^{ox} are given by

$$\sigma^{ex} = \left(1 - \frac{\partial f_e}{\partial \varepsilon^e}\right)^{-1}_{\varepsilon^e=\varepsilon} \frac{\partial F'_e}{\partial E'} \left(\frac{X_L}{X}\right)^2, \tag{6.10}$$

$$\sigma^{mx} = \left(1 - \frac{\partial f_m}{\partial \mu^m}\right)^{-1}_{\mu^m=\mu} \frac{\partial F'_m}{\partial H'} \left(\frac{X_L}{X}\right)^2, \tag{6.11}$$

$$\sigma^{ox} = \left(1 - \frac{\partial f_o}{\partial (n^2)^o}\right)^{-1}_{n^o=n} \frac{\partial F'_o}{\partial \mathcal{E}'} \left(\frac{X_L}{X}\right)^2, \tag{6.12}$$

f_e being determined by eq. (6.5), while

$$f_m = 4\pi \frac{N}{V} a^m \frac{\partial F'_m}{\partial H'}, \quad f_o = 4\pi \frac{N}{V} a^o \frac{\partial F'_o}{\partial \mathcal{E}'}, \tag{6.13}$$

with $a^m = \frac{1}{3} a^m_{ii}$ and $a^o = \frac{1}{3} a^o_{ii}$ denoting the mean diamagnetic and optical polarizability, respectively, of a molecule of the medium in the absence of a polarizing field; X is the intensity of one of the *external* polarizing fields, and X_L — that of the *local* polarizing field arising within the dielectric through the effect of the external field X.

Computation of theoretically predicted values of as yet undetected effects. The effects $\Delta(n^2)^e_{sat}$, $\Delta(n^2)^m_{sat}$ and $\Delta\varepsilon^e_{sat}$ have been detected experimentally and investigated for some time (see Introduction). All the remaining effects given by eqs. (6.6) — (6.8) still await detection and experimental investigation. Thus, it may be useful to assess their respective numerical values from the present theory, using the experimental values of the constants $\Delta(n^2)^e_{sat}$ and $\Delta(n^2)^m_{sat}$ of the known effects. The latter are those of Kerr and Cotton-Mouton, for which the respective constants of birefringence K and C are defined by

$$K \equiv \frac{n_{\parallel} - n_{\perp}}{n} \frac{1}{E^2}, \quad C \equiv \frac{n_{\parallel} - n_{\perp}}{n} \frac{1}{H^2}, \tag{6.14}$$

wherein $n_{\parallel}$ and $n_{\perp}$ are the values of the refractive indices for the vector of the measuring field parallel and perpendicular to that of the polarizing field.

By eqs. (6.8),

$$K = \frac{1}{2n^2} (S^{oe}_{\parallel} - S^{oe}_{\perp}), \quad C = \frac{1}{2n^2} (S^{om}_{\parallel} - S^{om}_{\perp}); \tag{6.15}$$

alternatively, by eqs. (6.9) and (4.19),

$$K = \frac{3\sigma^{oe}}{2n^2} \frac{B^{oe}_M}{V_M}, \quad C = \frac{3\sigma^{om}}{2n^2} \frac{B^{om}_M}{V_M}, \tag{6.16}$$

with B^{oe}_M and B^{om}_M denoting the molar constants of optical birefringence in an electric or magnetic field, as given in general by eqs. (4.20) and (4.21), while σ^{oe} and σ^{om} are the parameters determined by eq. (6.12). All parameters σ^{em}, ... σ^{oo} appearing in the foregoing equations may be computed theoretically from their definitions (6.10) - (6.12) assuming for the medium under consideration the appropriate model of the local field existing therein.

Assuming the model of Lorentz (1916), the local fields are of the form

$$\boldsymbol{F}_e = \frac{\varepsilon + 2}{3} \boldsymbol{E}, \quad \boldsymbol{F}_m = \frac{\mu + 2}{3} \boldsymbol{H}, \quad \boldsymbol{F}_o = \frac{n^2 + 2}{3} \boldsymbol{E}, \tag{6.17}$$

whence

$$\begin{gathered} \sigma^{ee} = \left(\frac{\varepsilon + 2}{3}\right)^4, \quad \sigma^{mm} = \left(\frac{\mu + 2}{3}\right)^4, \quad \sigma^{oo} = \left(\frac{n^2 + 2}{3}\right)^4, \\ \sigma^{em} = \sigma^{me} = \left(\frac{\varepsilon + 2}{3}\right)^2 \left(\frac{\mu + 2}{3}\right)^2, \\ \sigma^{mo} = \sigma^{o.n} = \left(\frac{\mu + 2}{3}\right)^2 \left(\frac{n^2 + 2}{3}\right)^2, \\ \sigma^{oe} = \sigma^{oe} = \left(\frac{n^2 + 2}{3}\right)^2 \left(\frac{\varepsilon + 2}{3}\right)^2. \end{gathered} \tag{6.18}$$

If considerations be restricted to the purely orientational effect and to molecules possessing the axial symmetry, eqs. (6.6) — (6.8) together with (5.15) — (5.20) may be expressed by the constants K and C of (6.14) — (6.16). Thus, assuming the Lorentz model (6.17) and (6.18), the equations yielding the six effects as yet experimentally not detected take the form

$$\Delta \varepsilon^m_{sat} = (3 \cos^2 \Omega_{em} - 1) \frac{2n^2}{3} \left(\frac{\mu + 2}{n^2 + 2}\right)^2 \frac{\mathscr{H}^m}{\mathscr{H}^o} K H^2, \tag{6.19}$$

$$\Delta \varepsilon^o_{tat} = (3 \cos^2 \Omega_{eo} - 1) \frac{n^2}{3} K \mathscr{E}^2_a, \tag{6.20}$$

$$\Delta \mu^e_{sat} = (3 \cos^2 \Omega_{me} - 1) \frac{2n^2}{3} \left(\frac{\mu + 2}{n^2 + 2}\right)^2 \frac{\mathscr{H}^m}{\mathscr{H}^o} K E^2, \tag{6.21}$$

$$\Delta \mu^m_{sat} = (1 + 2 \cos^2 \Omega_{mm}) \frac{2n^2}{3} \left(\frac{\mu + 2}{n^2 + 2}\right)^2 \frac{\mathscr{H}^m}{\mathscr{H}^o} C H^2, \tag{6.22}$$

$$\Delta \mu^o_{sat} = (3 \cos^2 \Omega_{mo} - 1) \frac{n^2}{3} C \mathscr{E}^2_a, \tag{6.23}$$

$$\Delta n^o_{sat} = (3 \cos^2 \Omega_{oo} - 1) \frac{n}{6} \left(\frac{n^2 + 2}{\mu + 2}\right)^2 \frac{\mathscr{H}^o}{\mathscr{H}^m} C \mathscr{E}^2_a, \tag{6.24}$$

where:

$$K = \frac{(n^2+2)^2(\varepsilon+2)^2}{54n^2}\frac{B_M^{oe}}{V_M}, \qquad (6.25)$$

$$C = \frac{(n^2+2)^2(\mu+2)^2}{54n^2}\frac{B_M^{om}}{V_M}. \qquad (6.26)$$

The effects defined by eqs. (6.19) — (6.24) will now be numerically evaluated for nitrobenzene from the experimental data at 20° C:

$$\begin{aligned} \varepsilon &= 34.3, & n^2 &= 2.43, \\ \mathcal{H}^o &= 7.3 \times 10^{-24}, & \mathcal{H}^m &= 1.3 \times 10^{-28}, \\ K &= 1.3 \times 10^{-9}, & C &= 9.3 \times 10^{-17}. \end{aligned}$$

With the Lorentz model, eqs. (6.19) — (6.24) yield

$$\begin{aligned} \Delta\varepsilon^m_{sat} &= 1.8\,(3\cos^2\Omega_{em} - 1) \times 10^{-14} H^2, \\ \Delta\varepsilon^o_{sat} &= 1.2\,(3\cos^2\Omega_{eo} - 1) \times 10^{-9} \mathcal{E}_a^2, \\ \Delta\mu^e_{sat} &= 1.8\,(3\cos^2\Omega_{me} - 1) \times 10^{-14} E^2, \\ \Delta\mu^m_{sat} &= 1.4\,(1 + 2\cos^2\Omega_{mm}) \times 10^{-21} H^2, \\ \Delta\mu^o_{sat} &= 0.8\,(3\cos^2\Omega_{mo} - 1) \times 10^{-16} \mathcal{E}_a^2, \\ \Delta n^o_{sat} &= 3.1\,(3\cos^2\Omega_{oo} - 1) \times 10^{-12} \mathcal{E}_a^2. \end{aligned} \qquad (6.27)$$

From this set of formulas it may be concluded that, using modern equipment, it should be possible experimentally to detect the effects $\Delta\varepsilon^m_{sat}$ and $\Delta\varepsilon^o_{sat}$, besides the one, Δn^o_{sat}, already predicted by Buckingham (1956). As a matter of fact, for nitrobenzene subjected to the effect of a magnetic field of 4×10^4 Oe parallel to the electric measuring field, the theory yields a value of $\Delta\varepsilon^m_{sat} = 6 \times 10^{-5}$. This represents an effect accessible to measurement, though the difficulties to be overcome are very great considering the simultaneous by-effects (as, e. g. the rise in temperature of the liquid brought about by the eddy currents in the condenser plates). Such experiments are being performed in this Laboratory, using modern techniques.

The second of the effects accessible to detection, $\Delta\varepsilon^o_{sat}$, amounts to as much as 1×10^{-5} if $\mathcal{E}_a^2 = 4.2 \times 10^3$ erg/cm³, i.e. if $\mathcal{E}_a = 19.5$ kV/cm. An electromagnetic wave beam whose electric vector is of such great intensity should have energy density amounting to $\varepsilon\,\mathcal{E}_a^2/8\pi$ or a luminous flux of $(cn/8\pi)\,\mathcal{E}_a^2 = 10^6$ W/cm². The latter could be obtained only as a short flash, by discharging a high voltage condenser battery through a gas.

Appendix

The rather involved calculations in the method proposed by the present authors will be exemplified by one of the consecutive steps, namely, the one leading to the computation of the statistical mean value of the component of the magnetic moment of a molecule of the diamagnetic medium in the direction of the measuring field $\boldsymbol{H}'$, in the presence of an electric polarising field $\boldsymbol{E}$:

$$\langle m_{H'} \rangle_{H',E} = \frac{\int\int \ldots \int m_i^m (\tau, \boldsymbol{H}', \boldsymbol{E})^{(p)} \beta_i^{(p)} e^{-\frac{\sum\limits_{p=1}^{N} u(\tau, \boldsymbol{H}', \boldsymbol{E})^{(p)}}{kT}} d\tau_1 \, d\tau_2 \ldots d\tau_N}{\int\int \ldots \int e^{-\frac{\sum\limits_{p=1}^{N} u(\tau, \boldsymbol{H}', \boldsymbol{E})^{(p)}}{kT}} d\tau_1 \, d\tau_2 \ldots d\tau_N} \, ; \qquad \text{(I)}$$

here, $m_i^m (\tau, \boldsymbol{H}', \boldsymbol{E})^{(p)}$ and $u(\tau, \boldsymbol{H}' \boldsymbol{E})^{(p)}$ denote the magnetic moment and the potential energy of the p-th molecule of the diamagnetic medium as given by eqs. (3.1) and (3.2), respectively. The directional cosines of the angles subtended by the axes of the molecular system of reference attached to the p-th molecule of the medium and the direction of the magnetic measuring field $\boldsymbol{H}'$ or of the electric polarizing field $\boldsymbol{E}$ are denoted by $\beta_i^{(p)}$ and $\alpha_i^{(p)}$, respectively.

Assuming, by analogy with eq. (2.7), that

$$F'^{(p)}_{mi} = F'_m \beta_i^{(p)}, \qquad F_{ei}^{(p)} = F_e \alpha_i^{(p)},$$

and on expanding in powers of the magnetic and electric fields, eq. (I) yields

$$\begin{aligned}
\langle m_{H'}^m \rangle_{H', E} = {} & \langle a_{ij}^{m(p)} \beta_i^{(p)} \beta_j^{(p)} \rangle F_m + \ldots + \frac{1}{2} \Bigg\{ \langle c_{ij,kl}^{me(p)} \beta_i^{(p)} \beta_j^{(p)} \alpha_k^{(p)} \alpha_l^{(p)} \rangle + \\
& + \frac{2}{kT} \left(\left\langle \sum_q b_{ij,k}^{me(p)} \mu_l^{(q)} \beta_i^{(p)} \beta_j^{(p)} \alpha_k^{(p)} \alpha_l^{(q)} \right\rangle - \langle b_{ij,k}^{me(p)} \beta_i^{(p)} \beta_j^{(p)} \alpha_k^{(p)} \rangle \left\langle \sum_q \mu_l^{(q)} \alpha_l^{(q)} \right\rangle \right) + \\
& + \frac{1}{kT} \left(\left\langle \sum_q a_{ij}^{m(p)} a_{kl}^{e(q)} \beta_i^{(p)} \beta_j^{(p)} \alpha_k^{(q)} \alpha_l^{(q)} \right\rangle - \langle a_{ij}^{m(p)} \beta_i^{(p)} \beta_j^{(p)} \rangle \left\langle \sum_q a_{kl}^{e(q)} \alpha_k^{(q)} \alpha_l^{(q)} \right\rangle \right) + \\
& + \frac{1}{k^2 T^2} \Bigg(\left\langle \sum_{qr} a_{ij}^{m(p)} \mu_k^{(q)} \mu_l^{(r)} \beta_i^{(p)} \beta_j^{(p)} \alpha_k^{(q)} \alpha_l^{(r)} \right\rangle - \\
& - \langle a_{ij}^{m(p)} \beta_i^{(p)} \beta_j^{(p)} \rangle \left\langle \sum_{qr} \mu_k^{(q)} \mu_l^{(r)} \alpha_k^{(q)} \alpha_l^{(r)} \right\rangle + \\
& + 2 \langle a_{ij}^{m(p)} \beta_i^{(p)} \beta_j^{(p)} \rangle \left\langle \sum_q \mu_k^{(q)} \alpha_k^{(q)} \right\rangle \left\langle \sum_r \mu_l^{(r)} \alpha_l^{(r)} \right\rangle - \\
& - 2 \left\langle \sum_q a_{ij}^{m(p)} \mu_k^{(q)} \beta_i^{(p)} \beta_j^{(p)} \alpha_k^{(q)} \right\rangle \left\langle \sum_r \mu_l^{(r)} \alpha_l^{(r)} \right\rangle \Bigg) \Bigg\} F'_m F_e^2 + \ldots, \qquad \text{(II)}
\end{aligned}$$

wherein the statistical mean values symbolized by the brackets $< >$ are those computed in the absence of external fields ($\boldsymbol{H}' = \boldsymbol{E} = 0$), and are defined by eq. (2.9).

In the absence of external fields, the various orientations of the p-th molecule with respect to the laboratory referential of the medium are all equally probable. Hence, in the expansion (II), it is permissible to average the directional cosines $\beta_i^{(p)}$,

... $\alpha_l^{(r)}$ separately and isotropically over all the possible orientations of the p-th molecule of the medium with respect to that system of reference. To do this, the directional cosines of the q-th and r-th molecules should first be expressed as functions of those of the p-th molecule by the transformation formulas

$$\alpha_k^{(q)} = \omega_{\sigma k}^{(pq)}\, \alpha_\sigma^{(p)}, \qquad \alpha_l^{(r)} = \omega_{\tau l}^{(pr)}\, \alpha_\tau^{(p)};$$

in the case under consideration, when the molecular systems of reference attached to the various molecules are rectangular, the coefficients of the transformation: $\omega_{\sigma k}^{(pq)}$, $\omega_{\tau l}^{(pr)}$, have the meaning of the cosines of the angles subtended by the axes of those systems. Thus, e. g., $\omega_{\sigma k}^{(pq)}$ is the cosine of the angle subtended by the σ-axis of the molecular systems of reference attached to the p-th molecule and the k-axis of that attached to the q-th.

By the foregoing transformation formulas and by eq. (5.14), the isotropic mean values of the functions of the directional cosines are

$$\overline{\alpha_i^{(p)}} = \overline{\beta_i^{(p)}} = \overline{\beta_i^{(p)}\, \beta_j^{(p)}\, \alpha_k^{(q)}} = \dots = 0,$$

$$\overline{\beta_i^{(p)}\, \beta_j^{(p)}} = \frac{1}{3}\, \delta_{ij}, \qquad \overline{\alpha_k^{(q)}\, \alpha_l^{(r)}} = \frac{1}{3}\, \omega_{kl}^{qr},$$

$$\overline{\beta_i^{(p)}\, \beta_j^{(q)}\, \alpha_k^{(r)}\, \alpha_l^{(s)}} = \frac{1}{30} \{2\,(2 - \cos^2 \Omega_{me})\, \omega_{ij}^{(pq)}\, \omega_{kl}^{(rs)} + \\ + (3 \cos^2 \Omega_{me} - 1)\, (\omega_{ik}^{(pr)}\, \omega_{jl}^{(qs)} + \omega_{il}^{(ps)}\, \omega_{jk}^{(qr)})\}, \qquad \text{(III)}$$

wherein δ_{ij} is the unit tensor of (2.4b), while Ω_{me} is the angle subtended by the vectors $\boldsymbol{H}'$ and $\boldsymbol{E}$.

With (III) and eq. (5.14), the expansion (II) takes the form

$$\langle m_{H'}^{m} \rangle_{H', E} = \frac{1}{3}\, a_{ii}^{m}\, F'_m + \frac{1}{90} \Bigg\{ 3\,(2 - \cos^2 \Omega_{me}) \left(c_{ii,jj}^{me} + \frac{2 b_{ij,k}^{me}\, \mu_l}{kT} \left\langle \sum_q \delta_{ij}\, \omega_{kl}^{(pq)} \right\rangle \right) + \\ + (3 \cos^2 \Omega_{me} - 1) \Bigg[3 c_{ij,ij}^{me} + \frac{6 b_{ij,k}^{me}\, \mu_l}{kT} \left\langle \sum_q \delta_{ik}\, \omega_{jl}^{(pq)} \right\rangle + \\ + \frac{a_{ij}^{m}\, a_{kl}^{e}}{kT} \left\langle \sum_q (3\, \omega_{ik}^{(pq)}\, \omega_{jl}^{(pq)} - \delta_{ij}\, \delta_{kl}) \right\rangle + \\ + \frac{a_{ij}^{m}\, \mu_k\, \mu_l}{k^2\, T^2} \left\langle \sum_{qr} (3 \omega_{ik}^{(pq)}\, \omega_{jl}^{(pr)} - \delta_{ij}\, \omega_{kl}^{(qr)}) \right\rangle \Bigg] \Bigg\}\, F'_m\, F_e^2 . \qquad \text{(IV)}$$

With the molar constant of magnetic saturation in an electric field defined as follows:

$$S_M^{me} \equiv \frac{4\pi}{3}\, \frac{N_A}{F_e^2} \left\{ \frac{\partial}{\partial F'_m} \langle m_{H'}^{m} \rangle_{H', E} - \left(\frac{\partial}{\partial F'_m} \langle m_{H'}^{m} \rangle_{H', E} \right)_{E=0} \right\}, \qquad \text{(V)}$$

eq. (IV) yields eqs. (3.3) and (3.4).

The molar constants of the remaining eight effects are computed similarly.

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