SCIENCE

VOL. LXIII JANUARY 15, 1926 No. 1620

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SCIENCE: A Weekly Journal devoted to the Advancement of Science, edited by J. McKeen Cattell and published every Friday by

THE SCIENCE PRESS

Lancaster, Pa. Garrison, N. Y.

New York City: Grand Central Terminal.

Annual Subscription, $6.00. Single Copies, 15 Cts.

SCIENCE is the official organ of the American Association for the Advancement of Science. Information regarding membership in the association may be secured from the office of the permanent secretary, in the Smithsonian Institution Building, Washington, D. C.

Entered as second-class matter July 18, 1923, at the Post Office at Lancaster, Pa., under the Act of March 8, 1879.

DIELECTRIC CONSTANT AND MOLECULAR STRUCTURE[1]

As I recall the scholarly and witty addresses delivered by my predecessors of the past *n* years, I am forced at the outset to confess to an inferiority complex of *n* dimensions. Three years ago Stewart initiated us into the mysteries of acoustical filters and made me wonder if it might not be possible to devise filters to exclude from our hearing those sounds made at night by the street cars and fire departments of Kansas City. Two years ago Saunders, though with characteristic modesty, made us all feel the importance and charm of spectroscopy. Last year Swann spoke on electrodynamics—I do not recall just what he said, but I remember the rapture with which I listened to this his "swan" song. I can not compete in wit or scholarship with these precedents, but I do claim a unique position in that I have the temerity to speak on a subject to whose development I have made no contribution, though I have encouraged some others to investigate it. In daring to speak on this subject, I fear that I place myself in a class with that officer, early in the war, who was commissioned to organize a committee to investigate one of the most highly technical and mathematical problems of the war and who carefully picked a committee of non-scientific men in order that its findings might not be prejudiced in favor of scientific methods of investigation.

My subject is "Dielectric Constant and Molecular Structure." Only twenty-five years ago the atomic structure of matter was held by some eminent scientists to be only a convenient hypothesis, accounting well for observed phenomena of chemistry and physics, but unsupported by direct unequivocal proof. In my college text-book of chemistry are the words: "It (the atomic theory) is not a statement of anything found by investigation. It is not an established fact. It may or may not be literally true, but . . . it furnishes a very convenient means of interpreting the facts of chemistry." Since that time atoms and molecules have been counted, individually weighed, dissected and their parts studied in many aspects. The question in these days is not, "Do molecules exist?" It is rather, "What is their structure and what forces hold their parts together and account for their properties?" In answer to this question we say

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[1] Address of the vice-president and chairman of Section B, American Association for the Advancement of Science, Kansas City, December 30, 1925.

unhesitatingly that every molecule consists of a certain number of atoms, each of which is composed of a known number of protons and electrons. We are less ready to specify the arrangement of the atoms within the molecules and are still less prepared to describe those forces which account for chemical union and physical properties, except in the most general way.

Assuming that the facts of chemistry tell us what atoms make up a molecule, let us review some methods of investigating further its structure. These methods are principally five in number.

(1) The ratio of the gaseous specific heat at constant pressure to that at constant volume is, on classical theory $(n+2)/n$, where n is the number of degrees of freedom which share in the thermal energy of the molecules. From this we are able to draw some conclusions regarding the structure of the simplest molecules, but this method is complicated by the fact that the energy is distributed according to quantum laws which approximate to the classical laws only in limiting cases, so that this method is of relatively little use.

(2) The arrangement of atoms in crystals, as found by X-ray diffraction methods, gives a clue to the geometrical arrangement of atoms in molecules, since it is reasonable to assume that the particular atomic force fields which account for the arrangement of atoms in crystals are responsible also for their arrangement in molecules.

(3) The molecular band spectra, as interpreted by the quantum theory, relate the frequency difference $\Delta\nu$ in the fine structure of a band to the moment of inertia I of the molecules by the relation $\Delta\nu = h/(4\pi^2 I)$. From the knowledge of I thus gained, the distances between the atomic nuclei in a number of biatomic and triatomic molecules have been determined. Furthermore, the frequency differences between band heads, and also the small variations of $\Delta\nu$ within a band, give some information regarding the degree of "firmness" with which these nuclei are held together.

(4) Phenomena such as molecular association, dissociation, ionization and adsorption indicate strong force fields around certain types of molecules, which presumably result from unsymmetrical arrangements of their electrical constituents. Typical molecules of this so-called "polar" class are H_2O, NH_3, HCl, SO_2, CH_3OH, while non-polar molecules are H_2, O_2, C_6H_6, CO_2.

(5) Particularly significant are phenomena occurring when molecules, by being placed in an electric field, are distorted or oriented. Under this heading we include refractivity and dielectric properties. In this address I wish to review the interpretation of specific inductive capacity, or dielectric constant, and call attention to the ways in which its study contributes to our knowledge of molecular structure.

Like many other things electrical, the clue to the interpretation of dielectric phenomena was given by Faraday, who pointed out that matter in an electric field should become electrically polarized by induction and thereby give rise to a field which would partially neutralize the applied field. Lorentz interpreted this induction in terms of modern ideas of molecular structure. Debye and J. J. Thomson pointed out a second factor contributing to dielectric action. Gans and Pauli have elaborated and refined the theory, and recent tests seem to have established its sound basis.

THEORY OF DIELECTRICS

Consider an electron which forms part of the structure of a molecule. If this molecule is placed in an electric field E the electron is displaced a distance s from its equilibrium position (or orbit. We shall speak of electron positions with the understanding that these are the time average positions). Whatever be the law of force which opposes this displacement, the shift may be taken as proportional to the displacing force for *small* displacements, and we may put $F = Ee = s/\gamma$ where γ is a binding constant related to the natural period of vibration of the electron T about its equilibrium position by the expression $T = 2\pi\sqrt{m\gamma}$. The displacement s is equivalent to the creation of an electric doublet of moment $\mu = es = Ee^2\gamma$. If there are N such displaceable electrons per unit volume, then the electric moment per unit volume is $P = NEe^2\gamma$, which is called the *polarization.* Since $P = (\varepsilon - 1)E/4\pi$, we have at once for the dielectric constant ε the expression

$$\varepsilon - 1 = 4\pi Ne^2\gamma. \tag{1}$$

This equation must be modified in view of several additional considerations.

(1) Not all electrons are similarly situated in the molecule. Suppose each molecule to contain ν_p electrons of type p, characterized by a binding constant γ_p and suppose that there are n types of electrons per molecule and N molecules per unit volume. We then have

$$\varepsilon - 1 = 4\pi Ne^2 \sum_1^n \nu_p \gamma_p. \tag{2}$$

(2) We have neglected the effect produced by the field of its neighbors on the electron displacement in each molecule. If intermolecular distances are large compared with molecular dimensions (as in gases), consideration of this interaction leads to

$$\frac{\varepsilon - 1}{\varepsilon - 1 + \alpha} = \frac{4\pi Ne^2}{\alpha} \sum_1^n \nu_p \gamma_p, \tag{3}$$

where $\alpha = 3$ for the random molecular arrangement in gases and liquids, but may have other values in solids. (3) We have neglected to consider the effect produced on the displacement of any electron by that of the other electrons in the same molecule. This is done by introducing a factor L_p, which is greater than unity, but probably not much greater so that it is generally neglected. The more general expression is therefore

$$\frac{\varepsilon-1}{\varepsilon-1+\alpha}=\frac{4\pi Ne^2}{\alpha}\sum_1^n \nu_p\gamma_p L_p \qquad (4)$$

This is, essentially, the theory of Lorentz. Since N equals the density D divided by the molecular mass M, and since $\alpha=3$ for liquids and gases, this expression may be written

$$\frac{\varepsilon-1}{\varepsilon+2}=AD, \qquad (5)$$

where A is a constant for any given substance. This is the well-known Clausius-Mossotti relation, which is very accurately true for some substances but which fails to account for variations with temperature observed with the so-called "polar" compounds.

If each molecule is a permanent electric doublet of moment μ, *i.e.*, if the center of charge of its constituent electrons does not coincide in position with that of its positive parts, then there is a tendency for molecules to orient themselves with their electric axes pointing in the direction of the applied field. This orientation is hindered by the kinetic reactions of thermal agitation, so that a certain statistical average degree of alignment results, which depends on the moment of the doublet, the strength of the field and the temperature. Boltzmann's theorem enables us to express the number of molecules oriented between angular limits ϑ and $\vartheta+d\vartheta$ with the field as

$$dN=CN\varepsilon^{\frac{\mu E\cos\theta}{kT}}\sin\vartheta\, d\vartheta$$

where C is a constant which is very readily evaluated, and k is the Boltzmann gas constant. Each of these molecules contributes an amount $\mu\cos\vartheta$ to the polarization P. By integration over all angles the total polarization from this cause is found to be

$$N\mu(\mu E/3kT+\mu^3E^3/45k^3T^3+\ldots)$$

in which the terms beyond the first are generally negligible. Including this polarization due to orientation of molecules with that due to the shift of electrons, we have the equation of Debye

$$\frac{\varepsilon-1}{\varepsilon+2}=4\pi N\left(\frac{e^2}{3}\sum_1^n \nu_p\gamma_p L_p+\frac{\mu^2}{9\,kT}\right)=\left(A+\frac{B}{T}\right)D. \quad (6)$$

Application to gases: In the case of gases this equation has only recently been tested with high accuracy, since the value of ε is so near unity that it must be determined with very high precision to give a significant value of $\varepsilon-1$. For instance an error of 0.001 per cent. in measuring ε leads to an error of 2 per cent. in $\varepsilon-1$ for nitrogen gas. Several satisfactory methods have recently been devised to take advantage of modern technique of high frequency circuits. One of these methods, first applied by Herweg and later improved by Zahn, consists in amplifying the electrical beats between two differently tuned oscillating circuits, one of which contains the experimental condenser which is alternately filled and emptied of gas. The electrical beats are made audible by a telephone receiver and produce acoustical beats with the sound from an electrically driven tuning fork. By always adjusting to zero beats and taking extraordinary precautions for shielding and steadiness, this method is capable of measuring a change in capacity of one part in two million.

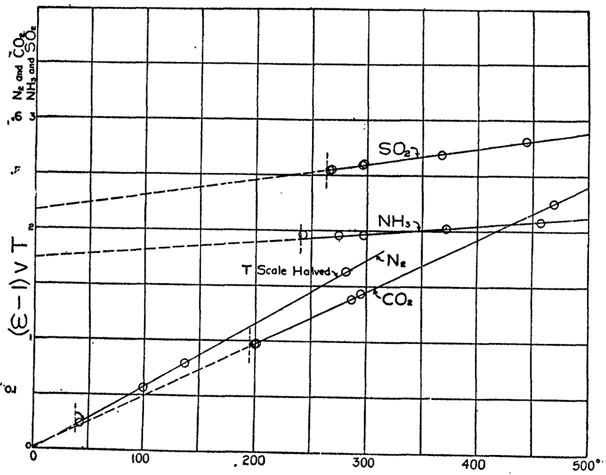


Figure 1 shows the variation of $\varepsilon-1$ with T. v is the reciprocal of the density, whence the result of plotting $(\varepsilon-1)\,v\,T$ against T should be a straight line if equation (6) is correct. (The factor $\varepsilon+2$ in these cases is constant within the limits of accuracy of plotting.) The slope of each straight line gives the quantity A, from which the "binding" constant γ may be computed, while the intercept gives the quantity B or the permanent electric moment μ of the molecule. Some of these moments are given in Table I.

Application to liquids: Debye's equation (6) does not describe very accurately the dielectric constant of liquids. Gans has shown that this is due chiefly to mutual actions between molecules which are not sufficiently allowed for in the approximate treatment of this effect used for gases, and has derived a much more complicated equation which reduces to equation (6) for fluids of low density like gases. This equation is apparently accurate for both liquids and gases (though a part of the mathematical analysis has been questioned) since it meets the most severe possible test: it permits the dielectric constant of the vapor

TABLE I

ELECTRIC MOMENTS μ OF MOLECULES

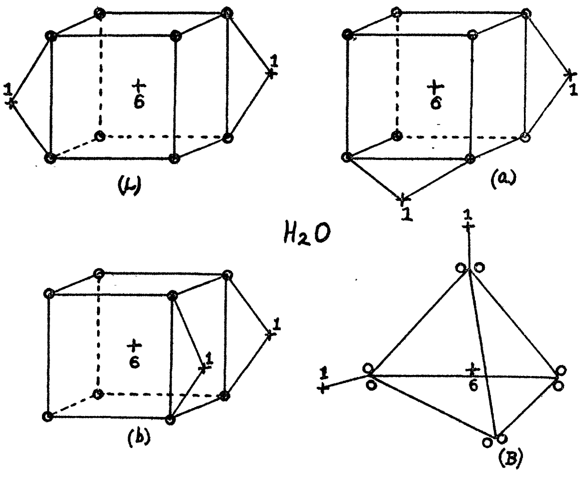
Gas[2]	μ	Liquid[3]	μ
HCl	1.03(10)$^{-18}$	H_2O	1.98(10)$^{-18}$
HBr	0.79	CH_3OH	1.78
HI	0.38	C_2H_5OH	1.85
NH_3	1.44	C_3H_7OH	1.98
SO_2	1.61	C_4H_9OH	2.06
H_2O	1.87	$C_5H_{11}OH$	2.15
C_2H_2	0.00	C_6H_6	0.20(?)
C_2H_4	0.00	$C_6H_5CH_3$	0.40
C_2H_6	0.00	$C_6H_5C_2H_5$	0.46
α C_4H_8	0.37	$(CH_3)_2O$	1.37
N_2	0.00	$C_2H_5)_2O$	1.37
CO_2	0.06	$(CH_3)_2S$	1.27

[2] Zahn.

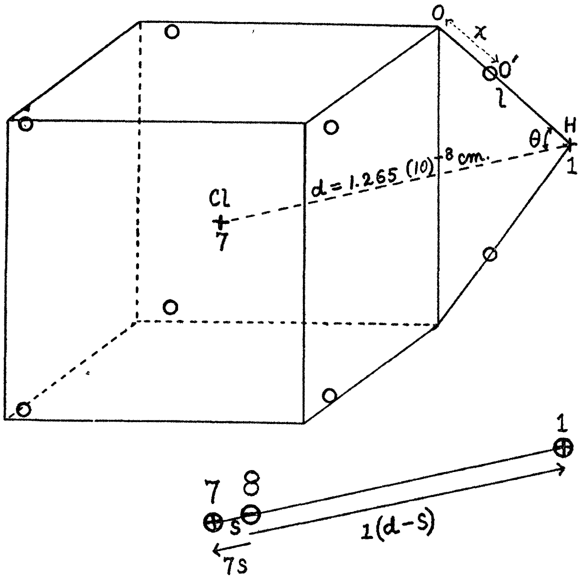
[3] Smyth.

accurately to be calculated from that of the liquid, or *vice versa,* for substances whose molecules do not associate in the liquid phase. For only a few liquids are data available for calculating the molecular electric moments from the Gans equation, but C. P. Smyth has shown how this may be combined with the Lorentz dispersion formula to permit at least an *approximate* calculation of the electric moment in many cases. Table I gives a few typical values, in which the probable error is much greater than in the case of gases.

In some cases the calculated value of the electric moment varies with temperature, which is apparently due to molecular association, since it occurs with those substances for which there is independent evidence of association. In fact Kalish has adapted Smyth's equations to estimate the degree of association in liquids at various temperatures. There is some indication that, in such cases, association disappears at the boiling point, but the evidence is inadequate to permit definite statement at present.



Some applications to molecular structure: Consider the familiar chemists' scheme for indicating the structure of a water molecule H-O-H. Or consider the more elaborate electronic configuration of the Lewis-Langmuir theory (L, Fig. 2). These arrangements are symmetrical in such a way that the center of charge of the electrons and that of the positive nuclei coincide at the center of mass of the molecule. Such molecules would have zero electric moment; yet the variation of dielectric constant with temperature shows that the water molecule is one of the strongest of molecular doublets. Therefore, among the possible arrangements and motions of the electrons and nuclei in a water molecule, we may exclude all symmetrical models and consider only those models which can give the proper electric moments. Furthermore, the band spectrum indicates more than one value for the moment of inertia, whence we infer that the three atomic nuclei are not situated on the same straight line. Models (a), (b) or (B) would satisfy the requirements of both dielectric constant and band spectrum as far as we can tell. Thus the consideration of dielectric constants may be used to *test* molecular models, but will not explicitly *give* us the models.



Consider further the hydrogen chloride molecule HCl. To illustrate the argument, take the Lewis-Langmuir model (Fig. 3), although the argument is general for any model. The chlorine nucleus and inner electrons give a net charge of +7 within an outer group of eight electrons whose mean positions may, to a first approximation, be the corners of an octet, while the hydrogen nucleus is symmetrically bound to electrons at two adjacent corners of the cube. The distance d between the Cl and H nuclei is known to be 1.265(10)$^{-8}$ cm, from the moment of inertia as given by the band spectrum. If the eight electrons were symmetrically situated about the Cl nucleus, the resultant charge of the entire cube would be equivalent to that of one electron at the center. This, together with the H nucleus, would constitute an electric doublet of moment $\mu = ed = 6.039(10)^{-18}$ c. g. s. But the presence of the H nucleus distorts the cube by attracting the electrons to new positions of equilibrium, indicated by the circles. Thus the center of charge of the electron system is shifted by an amount s toward the H nucleus. The system of charges is therefore equivalent to $+7$, -8 and $+1$ situated as indicated below in the figure. The resultant electric moment, as indicated by arrows, is $\mu = e(d - 8s)$. Since d is known from band spectrum data and μ from dielectric constant data, we may calculate the average shift s to be $0.13(10)^{-8}$ cm, which is a reasonable value.

Now there is an entirely independent method of calculating this shift s of the electron configuration, also based on the theory of dielectrics. The constant γ in equation (6) is the electronic shift per unit distorting force and may be evaluated from the constant A if we make the close approximation of considering the entire polarization of the molecule as due to the outer eight valence electrons. For HCl we thus find that $\gamma = 1.41(10)^{-6}$ cm/dyne. Now if we knew the exact configuration and dimensions of the electron structure we could consider each electron individually, compute its shift x due to the attraction of the H nucleus and average for all eight electrons the component of this shift in the direction of the molecular axis—thus finding s. Not knowing the configuration accurately enough for this, we may make a first approximation by supposing that this average shift will be the same as if all electrons were initially located at their unshifted average position at the cube center Cl, and then calculate the shift by the equation $e^2/(d-s)^2 = s/\gamma$. Thus we find $s = 0.26(10)^{-8}$ cm. These two methods of calculating s agree as to order of magnitude, but the second method gives a larger value. The approximations regarding location of the electrons and linear relation between force and shift over the entire shift x may account for such discrepancy as exists.

Other examples of applications of the theory might be cited, but I shall heed the Golden Rule and hasten on. The first term in the Debye equation, the term involving the binding constant A, is identical with the first term of the Lorentz optical dispersion formula. Thus the binding constant γ may be calculated from refractivity data, which are much more extensive than are dielectric constant data, and are available for ions in solution as well as for neutral molecules. Born and Heisenberg, Fajans and Jooz, Smyth and others have thus calculated the "binding constant" (or its equivalent, the "deformability") of various electron configurations. Some of these are shown in Table II.

TABLE II

SYSTEMS OF EIGHT DISPLACEABLE ELECTRONS

	O^{--}	F^{-}	Ne	Na^{+}	Mg^{++}	A^{+++}	Si^{++++}
Ion core	+6	+7	+8	+9	+10	+11	+12
$\gamma(10)^6$	1.52	0.54	0.22	0.108	0.062	0.037	0.022

Atom	He	Ne	A	Kr	Xe
$\gamma(10)^6$	0.43	0.22	0.91	1.37	2.25

Molecule	HF	HCl	HBr	HI
$\gamma(10)^6$	0.41	1.41	1.96	2.91

γ is the displacement per unit force.

We see that the electrons are most easily shifted in ions with small central positive charges (cores) and also in large atoms, where they are far removed from the center.

This deformability has a very important bearing on the theory of spectra. Consider, for example, the spectrum of sodium. We are accustomed to think of the valence electron as executing an approximately elliptical orbit about the central core, subject to the attraction of the $+9$ charge at the center and the repulsion of the -8 charge of the outer electron group. A general consideration of the motion of the valence electron in such a field of force leads to a spectral series formula of the Ritz type

$$\nu = R\left(\frac{1}{(n^1 + k^1 + \ldots)^2} - \frac{1}{(n + k + \ldots)^2}\right)$$

in which the terms k arise from the repulsive non-central character of the field due to the outer electron shell. While formally acceptable, this picture is physically untenable since it leads to the wrong algebraic sign for the terms k. Stated physically, the departure from a central force field must be in the direction of an *attraction* rather than a *repulsion* on the valence electron.

Born and Heisenberg and Jones and Boyce have pointed out that such an attraction should result from the distortion of the electron shell in the field of the valence electron. This distortion, when the valence electron is distant r, amounts to a shift $s = \gamma e^2/r^2$ making the atom core a doublet of moment $\mu = 8se$ which attracts the valence electron with a force $2\,\mu e/r^3$ or $16\,\gamma e^4/r^5$. When this force, thus computed with the aid of γ given by refractivity or dielectric constant data, is included in deriving the Ritz series formula, the theoretical values of k are found to agree rather acceptably with the actual values for sodium and about a dozen other elements whose spectra are of similar type.

In concluding let me remind you that many other aspects of dielectric constant deserve more study. There are the phenomena of electric double refraction and of the variation of dielectric constant with field strength which should open the way to a study of the law of force by which the electrical constituents of molecules are held together. There is the study of refractivity of particular electron groups and of chemical radicals, which can shed much light on the atomic arrangements in complicated molecules. There is the interesting question of the conditions of pressure and temperature at which the classical theory of dielectrics fails and a quantum theory must be employed—and of the nature of this quantum theory. There are innumerable problems of the effects of the strong local force fields of dipole molecules on such properties as heat of sublimation, association, dissociation, ionization, adsorption, conductivity, osmotic pressure, residual valency, electrical double layers, and so on. While all these have been pretty definitely related to deformability of molecules or to their electric doublet character, the field is an open one for research which will render more precise our understanding of this group of phenomena.

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ANOTHER OUTLOOK ON THE CHEMICAL REGULATION OF RESPIRATION[1]

The regulation of respiration is a subject which is engaging the attention of physiologists, but the fluctuations of respiration in numerous pathological conditions have a significance which must likewise hold the interest of clinicians. I have, therefore, attempted to review a theory which seems at present to offer the most complete explanation of respiratory phenomena.

When respiration is suspended three outstanding changes in the arterial blood occur: an increase in the carbon dioxide tension; an increase in the hydrogen ion concentration and a decrease in the oxygen tension. When respiration is resumed the blood returns to its normal condition, and the conscious desire to breathe disappears. Such observations suggest that any one of these changes may be the factor controlling respiration, and several theories have been proposed explaining the chemical mechanism of respiratory control. According to one theory the respiratory center is stimulated by the free hydrogen ions of the arterial blood; according to another theory by a specific action of carbon dioxide, and according to another by a lack of oxygen in the arterial blood.

Several years ago my studies on the volume-flow of blood led me to doubt the prevailing theories of respiratory control, for I found that respiration could be stopped by simply accelerating unchanged blood through the respiratory center. Such experiments definitely indicate that the metabolism of the respiratory center itself and the volume-flow of blood through the center are important factors which must be considered in the ultimate explanation of the regulation of pulmonary ventilation. These conclusions are the result of a great number of diverse experiments devised to explain the harmful effects of hemorrhage and the beneficial effects of subsequent injection of non-nutrient solution.

In the submaxillary gland of the dog hemorrhage elicits a profound change in the volume-flow of blood. A 10 per cent. reduction of blood-volume may elicit a 65 per cent. reduction in the normal flow of blood. On reinjection of an equal amount of gum-saline solution the volume-flow may return to normal. The nutrient-flow (volume-flow × concentration of nutrients in the blood) necessarily increases.

Assuming that the function of a tissue is dependent on the nutrient-flow—hemorrhage and subsequent injection should affect the activity of the gland. Direct experiments show that a continuous secretion of saliva elicited by the intravenous injection of pilocarpin is diminished by hemorrhage and increased by subsequent injection of gum-saline solution.[2]

Observations led me to believe that the conditions in the submaxillary gland hold for the body as a whole and explain the general beneficial effects of injection of inert solution. Nevertheless, experiments were extended to other tissues as well and the same results were obtained.

In muscle, which comprises the bulk of the mammalian organism, hemorrhage and injection elicit like changes in volume-flow of blood. Similarly, the ability of the muscle to respond to repeated stimulation is diminished by hemorrhage and improved by subsequent injection of gum-saline solution.

The basal metabolism of the organism as a whole is likewise affected by hemorrhage and injection. Hemorrhage diminishes and subsequent injection of inert solution increases basal metabolism.

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[1] From the Department of Physiology, University of Michigan, Ann Arbor, Michigan.

[2] Though on the whole during acute experiments gum-saline solution appears to improve the general nutrition and function of various tissues, the greatest care should be exercised in the use of this blood substitute in man. Extremely toxic effects with a large drop in blood pressure were not uncommon, even though a high grade of gum acacia and methods of purification were employed.