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MOLECULES[1]

By Professor N. V. SIDGWICK

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IT is commonly assumed that chemistry, like physics, can prevail everywhere, but on inquiry it can be readily seen that this is by no means so; it is only under rather exceptional conditions that chemical processes can occur. This is a matter which concerns every one, and not chemists alone, because it is only where chemistry is possible that life is possible. Indeed, that is one reason why the limitations of chemistry have not always been recognized, because we are enclosed within the same limits ourselves.

Chemistry is commonly called molecular physics: it is the investigation of the structure and behavior of those little groups of atoms which we call molecules, whose almost infinite repetition constitutes the chemical substances of our ordinary experience. The first point therefore is to know what molecules are, and in general terms why they are formed.

[1] The Maiben Lecture delivered before the meeting of the American Association for the Advancement of Science, Denver, June 23, 1937.

The matter of the universe consists of atoms, of some 90 to 95 different elements. Each atom is made up of a small positively charged nucleus, surrounded by a number of electrons equal to the number of units of positive charge on the nucleus. Now the electrons surrounding a nucleus can arrange themselves in groups of greater or less stability, and it often happens that two or more atoms can make a more stable arrangement of their electrons by pooling them or by transferring some of them from one atom to the other. If the extra stability so gained is great enough, the atoms will remain attached to one another, and a molecule will have been formed. It is only a few of the outermost electrons of any atom which take part in these rearrangements—the greater number are already sorted out into groups—and in consequence the number of atoms which forms a molecule is never large, often only two or three, and rarely more than a hundred.

It is the business of chemists to examine the behavior, both physical and chemical, of molecules, to determine with the help of the physicists their structures, and to find the relations between the structures and the properties.

If this is so, the first thing that is obvious is that chemistry can only occur where there are molecules, and that chemical processes can only occur where these molecules react with one another. This imposes definite limits on the sphere of chemistry, limits which in a sense are surprisingly narrow. We can arrive at an idea of these limits in two ways, either by direct observation or by deduction from the general principles of physics; as I hope to be able to show, the results of these two methods agree. For the observational method we have to rely on astronomy, except so far as this globe is concerned. The progress of that science during the last hundred years has shown that the composition of the matter in all parts of the universe is much the same, that the stars are made up of the elements which we know on earth, and that the same laws of nature hold elsewhere as we find here. Thus we can apply our knowledge of the behavior of matter on the earth to other parts of the universe with a fair prospect of success.

The most obvious characteristic in which different stars differ is their temperature. The heat of a body is due to the agitation of its molecules, and the energy of this agitation is proportional to the temperature. Throughout the universe the temperature varies widely, from a very few—say two or three—degrees above the absolute zero in empty space, or in very old or very small stars such as the moon, up to several millions (even hundreds of millions according to some physicists) of degrees in the center of large stars like the sun.

Our knowledge of the composition of the stars (and much of our knowledge of their temperatures, too) is derived from the study of their spectra; every element or compound has a characteristic spectrum, and from either the light emitted by a star or that absorbed when light from another source passes through its atmosphere, we can discover the nature of the substances composing that atmosphere. The story of the way in which these problems have been solved is a most fascinating one, but it would take too long to discuss it here; on the molecular side the fundamental work is largely due to Rupert Wildt in Germany, but much of the conclusions have been worked out by Professor H. N. Russell, of Princeton, who has described them in his Halley Lecture (Oxford, 1933) and more especially in the address which he gave at Pittsburgh as the retiring president of this Association.[2]

[2] Printed in *Nature*, 135: 219, 1935; SCIENCE, 81: 1–9, 1935.

From these investigations it appears that in the sun's atmosphere with a temperature in the parts we can see of about 6,000° Abs., there are practically no molecules at all; even those which are most stable at high temperatures, such as the cyanogen radical CN, can scarcely be detected. We may therefore take this temperature of 6,000° Abs. as being the highest temperature at which chemistry can exist. This is nearly twice the temperature of the electric arc, which is the highest temperature that we can produce artificially in any considrable space. At any temperature lower than this we shall find molecules existing wherever there is matter.

But at these low temperatures, say at the boiling point of liquid air—180° C. or 100° Abs.—though there must be plenty of molecules, there will be very little chemistry. Chemistry implies not only the existence but also the reactions and interconversions of molecules, and we can show that at such low temperatures the great majority of molecules do not react.

It is therefore evident from our observation of the behavior of matter that the scope of chemistry in the universe is strictly limited; it can exist only where it is neither too hot nor too cold. Moreover, these limits are fairly narrow. The temperature of different parts of the world varies, as we have seen, from about 2° Abs. in interstellar space to at least 40 million and perhaps as much as 1,000 million in the centers of some stars, that is, in the ratio of 20 millions, or perhaps 500 millions, to one, or, in the terminology of the musical scale, over 24 octaves on the lower estimate and 30 octaves on the higher. The range over which we may consider chemical reaction to be possible to any considerable extent is from 100° Abs., the boiling point of liquid air, to 6,000°, the temperature of the outer layers of the sun's atmosphere, and this is a ratio of 60 : 1, or less than 6 octaves—say from a quarter to a fifth of the whole scale.

It is thus clear that the phenomena of chemistry are not universally diffused; they are confined to particular parts of the world where it is neither too hot for molecules to exist nor too cold for them to react. If these considerations merely defined the province of the chemist, we might say that they were of small interest to any but chemists; but they go much further than this. It is quite clear that without chemistry there can be no life. Even the simplest of living organisms are made up of molecules of great complexity, and their life depends on the occurrence of chemical changes among these molecules. Living organisms can endure very diverse conditions, but the limits between which molecules can exist and react are final. It is only within them that life can be carried on.

As these limits are so important, it is worth while to examine them rather more closely, and inquire what is the reason for their existence—why molecules are all destroyed above 6,000° and cease for practical purposes to react below 100°. The temperature, which is the decisive factor, is a measure of the agitation of the molecules; these are always in motion, and their energy, as measured in calories per gram-molecule, is almost exactly twice the average temperature. Hence the mean energy of thermal agitation of the molecules is 200 cals. at 100° Abs., and 12,000 cals. at 6,000°. But though this is the average energy, the energies of the individual molecules vary over a wide—theoretically an infinitely wide—range around this mean, the number that have any given energy being less, the more that energy departs from the mean. For example, the fraction of the molecules of a gas which have energies at least x times the mean will be 1/N, where x and N have the values given in Table I.

TABLE I

DISTRIBUTION OF ENERGY IN A GAS. ONE MOLECULE IN N HAS AT LEAST x TIMES THE AVERAGE ENERGY

$x =$	N =
2	$7 \cdot 4$
3	$20 \cdot 1$
5	$148 \cdot 6$
10	27,120
20	$4 \cdot 9 \times 10^{8}$
30	$1 \cdot 1 \times 10^{13}$
50	$5 \cdot 3 \times 10^{21}$
100	$2 \cdot 7 \times 10^{43}$

Incidentally it follows from this that in a liter of gas at the ordinary temperature and pressure there are about 5 separate molecules with 50 times the average energy, and that one molecule with 100 times the average energy occurs in it for one second in every 38 million million years.

Now it is obvious that there will be an end to the existence of any pair of molecules when they hit one another so hard as to break one another up, and this is essentially the reason why, as we have seen, they cease to exist at high temperatures. The amount of molecules present depends on the relative chances of their being formed and broken up, which is rather a complicated question; but we shall get an idea of their length of life if we consider how often at any given temperature a molecule will be struck with sufficient energy to disrupt it. The average energy required to break a link between two atoms (it does not vary very widely) is 70,000 calories per gram-molecule. The total number of collisions which a molecule of a gas or a liquid suffers in a second is very large; it varies with the mass, pressure and temperature; but for a molecule of air at the ordinary temperature and pressure it is $1 \cdot 2 \times 10^{9}$ per second. In a gas like air at 1 atmosphere we can calculate for any given temperature what is the total number of collisions that a molecule undergoes per second, and how many of these are violent enough to break it up. The answer is given in Table II, in which the successive columns give the absolute temperature, the number of collisions per second for air at that temperature, the number of effective collisions (*i.e.,* of energy at least 70,000 calories per gr. mol.), and finally, for the lower temperatures, the reciprocal of this last figure, the time before an effective collision occurs.

TABLE II

COLLISIONS IN AIR AT 1 ATMOSPHERE

T° Abs.	Collisions per sec.		1 Effective collision in
	Total	Effective	
500°	$1 \cdot 5.10^{9}$	$5 \cdot 9.10^{-22}$	$3 \cdot 7.10^{9}$ years.
1,000°	$2 \cdot 1$ "	$1 \cdot 3.10^{-6}$	16 hours.
2,000°	$2 \cdot 9$ "	73	1/73 sec.
3,000°	$3 \cdot 6$ "	29,800	
4,000°	$4 \cdot 1$ "	726,000	
5,000°	$4 \cdot 6$ "	4,210,000	
6,000°	$5 \cdot 1$ "	13,600,000	

It is clear from these figures why molecules tend to disappear as the temperature gets higher, and why at that of the sun's atmosphere they have practically ceased to exist.

Having seen that we get a satisfactory agreement between observation and calculation for the highest temperatures at which molecules can exist, we can now go to the other extreme and consider what is the lowest chemical level of temperature, that at which the reactions of molecules are so slow that they practically do not occur. It must be understood that we are now considering not merely destructive reactions involving the breaking up of a molecule, as we were before, but reactions in general, in which molecules combine with one another or take up or lose or exchange atoms.

This needs a little preliminary consideration of the conditions of chemical reaction in general. It is clear from what I have said about the frequency of collisions between molecules that any reaction in which two molecules always reacted when they met would be practically instantaneous: in other words, any chemical reaction which is slow enough to be measured must be one in which only a very few of the collisions cause reaction to occur. In our previous problem, which was concerned with reactions in which an atomic linkage was destroyed, it was easy to see that only the more energetic collisions would count; but we are now dealing with reactions in general, where there need not be any energy absorbed, but on the contrary energy may be evolved. Even here, if the rate of reaction is not too quick to measure, we can see that only a small proportion of the hits can cause chemical change. There must then be some difference in character between a collision which is fruitful, that is, which leads to reaction, and another collision which is not. This is obviously the difference in energy which we have already discussed. Before two colliding molecules can react they must have a certain amount of energy, which in all but very rapid reactions is much more than the normal molecule has, and is an amount that only very few of the molecules possess. The actual amount of this energy, which is known as the heat of activation, varies greatly, but its average value for the ordinary slow reactions is of the order of 30,000 cals. per gr. mol., which is not very different from that necessary to disrupt the ordinary link (70,000 cals. on the average), and so this line of argument leads to the same general conclusions as we have already reached. But from the further consideration of the process of reaction we get some interesting results. When two molecules react, as in

$$A_2 + B_2 = 2\,AB,$$

we have two changes occurring: the relative positions of the atoms change, and also the orbits of their electrons. When it was first realized that the linking of atoms in molecules is effected by means of the electrons, it was very naturally thought that the important process in the reaction, and the one for which the activation energy was needed, was this rearrangement of the orbits of these electrons. Further work has, however, shown that this is not so: the electronic rearrangements take place relatively easily as soon as the atomic nuclei have been brought into the proper positions, and it is for this latter purpose that the activation energy is mainly required. At first sight this movement of the atoms seems as if it should be easy. We commonly represent the atoms in a molecule by spheres in contact, and this gives us for this reaction the picture from which it would appear that

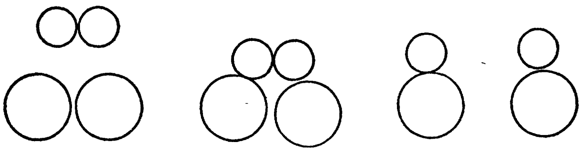

Fig. 1

the reaction should occur whenever two molecules met. This picture is, however, imperfect in a very important respect. We now know a great deal about the shapes and sizes of molecules, and one essential fact that we have learned is that the distance between two atoms linked together in the same molecule is very much shorter than that between the same two atoms when they are not linked, as when they are in different molecules, even when the molecules come as close to one another as they can. Taking the lighter atoms, with which in organic chemistry, and especially in biochemistry, we are mainly concerned, we may say that the average distance between two linked atoms is about $1 \cdot 5$ Ångström units (1 Å.U. $= 10^{-8}$ cm), while that between two neighboring but not linked atoms is about $3 \cdot 5$ Å.U.—more than twice as great. The difference is due to the fact that two unattached atoms repel one another because their outsides are formed of negatively charged electrons, but when these atoms are chemically linked this repulsion is overcome. If we use for our models, as I did just now, little spheres which are in contact when the atoms are linked, we may express this other effect by supposing that every atom on the unlinked side is surrounded by a sort of envelope about 1 Å.U. thick, separating it from other molecules. It is then clear why it is usually necessary for a molecule to have considerable energy before it can react: it must be able to penetrate this envelope, and get near enough to the other molecule for the new atomic linkage to be established.

This question of the existence of molecular envelopes and of heats of activation may seem to be of a rather unpractical kind or, as people outside universities say, of merely academic interest. But its interest is in fact extremely practical. These envelopes are of far greater importance to us than anything that courts or kings—or even Presidents—can cause or cure. We are all made up of compounds of carbon, hydrogen, oxygen and nitrogen, with a small amount of other elements. Now a system made up of these elements, if it has plenty of free oxygen, as we have in the air, when it has finished reacting is practically all converted into water, carbon dioxide and nitrogen. The only thing that prevents us from changing at once into these products is that the rate of reaction is slow, and we are able to repair the damage as fast as it occurs. But this slowness of reaction is due to the existence round our molecules of this molecular envelope. If that were removed the oxygen molecules would come up into position for reaction alongside of the organic molecules at every collision: every collision, and not merely as at present a few of the more energetic, would lead to oxidation, and we should all be burned up in a few moments.

This brings me to another question, that of the conditions under which life is possible. We have seen that it is only possible where there are molecules and where there is chemical change, and I have tried to show what the temperature limits of the occurrence of chemical change are. But it is evident that the conditions under which life as we know it is possible are much narrower than these. The complicated molecules which form the basis of living tissue can not exist up to 6,000° or react down to 100° Abs. A complicated molecule is always more easily destroyed than a simple one, because if it gets broken the parts are less likely to come together again.

But if we really want to know under what conditions life can exist, we must not pay too much attention to the forms of life which we know on earth, but must consider whether other forms of life may be possible, and whether there may be other conditions under which life can develop. As far as we can see, the existence in any material form of life, including in that term animals, that is, organisms which can move about freely (I don't think we are much interested in purely vegetable existences) requires four things: (1) organized living matter; (2) an external source of energy; (3) some unorganized and probably inorganic substance in the surroundings which can react with the living matter and give it the necessary energy; and (4) what I may call a lubricant, some probably inorganic substance liquid at the temperature of the animals, which makes their motions and their reactions possible. We may consider these four factors separately.

(1) *The organized living matter.* The material basis of all the forms of living matter that we know is a series of compounds of carbon. That is why the chemistry of carbon is known as organic chemistry. We have first to consider whether there is any other element that might take the place of carbon. There is only one that has ever been suggested as possibly capable of replacing carbon in living matter, and that is silicon. It has however been evident for some time that even silicon has not the properties which such an element needs. This makes our inquiry more precise, because we know something about the range of stability of carbon compounds, and the possibility of some entirely different material being employed is excluded.

(2) *The external source of energy.* If our animals are to do anything, they must acquire energy from somewhere. How this is done on the earth is familiar to all of us. The ultimate source of the energy is the sun's radiation, which enables plants to build up compounds of carbon from water and the carbon dioxide of the atmosphere; these compounds are eaten by animals, and in their bodies combine with the oxygen of the air, being reconverted into water and carbon dioxide and in the process liberating energy for the use of the animals. It is difficult to see what other method there can be which is anything like as convenient. The animals must have some external source of energy. Any chemical source, from the chemical combination of the unorganized world surrounding them, would very soon be used up, and the only steady source of supply we can imagine is the radiation from a star. If this is to be used, the living organism which is to absorb and transform it must have a very large surface in comparison with its mass. These are very unsuitable proportions for a creature that is to move about freely, which should be compact. Hence it is an obvious economy to separate the two functions: to have one kind of machine, which need not move about, with a large surface to absorb the radiant energy, and another which is adapted for motion but not for the absorption of radiant energy and which gets its energy by consuming the products of the first kind and reconverting them into the material of lower energy from which they were formed by the help of the radiation. The source of radiant energy will be the radiation from a hot star, which implies that the life must be confined in the main to the outside of the planet on which it occurs, and also that there must be in its neighborhood a hot star big enough and hot enough to supply the necessary radiation. This will normally be the star to whose system the planet belongs.

(3) *The energy-carrier.* The animal must have access to some substance which can combine with the product of the plant with the liberation of energy. It is difficult to think of anything which could replace oxygen for this purpose. It must be a substance which can exist in the gaseous or liquid surroundings of the organism and will not all combine with the solids. The only materials which meet these requirements are the gaseous elements and their volatile compounds, and the latter, such as water or ammonia, have not enough energy for the purpose. We are thus confined to oxygen, for nitrogen is far too inert.

(4) *The lubricant.* It is fairly obvious that life can not be carried on by creatures entirely composed of dry solids. Chemical reactions scarcely occur in solids, and as we all know mechanical operations are impossible without a lubricant. Hence the world where life is to be possible must contain a liquid which can interpenetrate the living matter. We can further see that the substance must be one which is liquid at the temperature of our living system, that is at temperatures which are not too high for the complicated organic compounds of living matter to exist. Practically the only common substances which will satisfy all these requirements are the lower hydrocarbons like methane and ethane, ammonia and water. The hydrocarbons are much too inactive; the atmosphere in which our animals live must contain oxygen, and this would rapidly burn up the ammonia to nitrogen and water. Hence the only available liquid which will support the activities of living creatures is water. So, the temperature limits of life on earth must be valid for life of any kind anywhere; the temperature must lie between limits which are only slightly outside the melting and boiling points of water.

To sum up, it would seem that life will be mainly confined to the surface of the planet on which it occurs, owing to the necessity of its receiving radiant energy. This planet must not be too small or the atmosphere will be lost, as has happened on the moon. On the other hand, it must not be too large: if its atmosphere is too dense, the radiation from which the life derives its energy will be cut off by the upper layers, and not enough will reach the surface, where practically all the living organisms must be. The prevalent temperature must be on the average between the boiling and the freezing point of water, though a slight excess or defect beyond these limits is possible. This is of course the most serious limitation of all. The freezing point of water is 273° Abs.; the boiling point depends on the atmospheric pressure, but as we must not have too dense an atmosphere we shall be safe if we say that the boiling point will not lie above 500° Abs. (227° C.), which is its value under 27 atmospheres pressure. This gives us a temperature range of only 500–300 or less than one octave out of the 24 or 30 octaves that occur in nature.

The application of these conclusions to the universe is a matter for the astronomers. The conclusions are not of course confined to the solar system, though there is a difficulty in applying them anywhere else, since all the stars that we can see are too hot, and life could only occur on their planets, which are too small to be visible. As far as the familiar planets of our own system are concerned, they only confirm the views that have long been held. The moon is much too small for life to be possible; Mercury is probably too small and too hot; Jupiter and the outer planets are too cold. The only places in the solar system where life is possible seem to be the earth and our two neighbors, Mars and Venus.

OBITUARY

FREDERIC E. IVES

FREDERIC EUGENE IVES, inventor, investigator, scientist, died on May 27, 1937, at his home in Philadelphia. His achievements were many and important, and were all the more remarkable in that he was essentially a self-educated man; he never attended a formal school after he was twelve years of age.

He was born on February 17, 1856, on a farm near Litchfield, Connecticut. His parents were descendants of the early New England settlers. From his father, Hubert Leverit Ives, a hard-working farmer, he inherited a capacity for concentrated application to which may be credited much of his success; from his mother, Ellen Amelia Beach, he derived a love of the artistic which doubtless stimulated his interest in the field of investigation which he chose for his own.

When he was twelve his father died, which interrupted his schooling and forced him to earn his living. After a brief and unsatisfactory experience as clerk in a country store he became apprentice in the printing office of the *Litchfield Enquirer*. The years spent in this newspaper office formed an excellent substitute for the schooling which he had missed and also gave him valuable training in preparation for his future career.

At this time he became interested in picture making both by the process of wood engraving and the art of photography. The limitations of the former method impressed him with the advantage of the photographic process and led him later to attack the problem of photo-engraving. His spare time, which was little, was spent in experiments in photography, his first camera being made, as he tells us, of a cigar box and a spectacle lens.

After completing his apprenticeship he worked for some time as a printer but soon turned to photography as his vocation. This led to his employment in 1874 by Cornell University, where he remained for four years in charge of the photographic laboratory. His contact with this institution doubtless stimulated his interest in the scientific aspect of his work and inspired his inventive genius. It is to these years that we refer his first notable achievement, the invention and the development of the first commercially successful half-tone process of photo-engraving.

The success of this invention, which has revolutionized the art of illustration, led him to connect himself with a printing establishment in Philadelphia in which he worked as a photo-engraver, maintaining at his home a private laboratory where he busied himself incessantly in numerous investigations which many times led to important inventions. Here in 1886 he developed the cross-line screen method of half-tone reproduction which is now universally used, superseding his earlier process. Here also he carried out the extensive experiments in color photography and color reproduction by the trichromatic process. His brilliant success in the solution of this problem by the invention in 1892 of the photochromoscope, or, as he called it, Kromskop, won for him recognition in the scientific world. This was perhaps his greatest achievement, and one in which he continued to work throughout his life, developing improved methods and new applications; as for instance to the moving picture industry, where the colored films shown at the present time are largely due to his inventions.

In addition to these accomplishments the work of Ives bore fruit in many other ways. Numerous devices, mostly in the field of optics, are due to his ingenuity. Among these may be mentioned an improvement in the binocular microscope, the parallax stereogram, diffraction grating replicas, a diffraction photochromoscope and a trichromatic colorimeter. Over seventy patents were taken out for his inventions, and as many more could easily have been obtained.

With exception of a few years in London and in New York spent in exploiting his inventions, the remainder of his life was passed in Philadelphia. He