

"Valence and Molecular Structure," Lecture 3. 1957. Produced for the Institutes Program of the National Science Foundation. Robert and Jane Chapin, producers.

Linus Pauling: This lecture is the first of three lectures on one part of chemistry - valence and the structure of atoms, molecules, and crystals. It was the British scientist Eddington who said that the study of the physical world, and I would say the biological world too, is a search for structure and not a search for substance. If we want to understand the human body, we must know its structure in terms of the cells that make it up. If we want to understand cells, we must know their structure in terms of molecules. If we want to understand molecules, we must know their structure in terms of atoms. And to understand atoms, we must know their structure in terms of electrons and nuclei - one nucleus down in the center of the atom with a number of electrons around. To understand nuclei, as the physicists are trying to do now, we must know, must learn their structure in terms of protons and neutrons and perhaps mesons. And it may well be that at sometime in the future, the fundamental particles, the electrons, protons, neutrons, mesons, will be found to have structure also in terms of still smaller particles that have not yet been discovered.

This subject - a branch of chemistry that correlates the multitude of facts of chemistry in an effective way and makes it easier for the student to learn and to remember the subject - this branch of chemistry is illustrated by the model that I hold here; a model showing the structure of ice. Here we have the hydrogen atoms, the oxygen atoms, the water molecules arranged together in space in a certain way. It is this arrangement, this structure, that accounts for the properties of ice. I hope to be able to come back to discussion of the structure and properties of ice later on.

Now, let us consider some substances and their properties that need to be explained in terms of structure. You all know the example of diamond and carbon. Both of these substances are made up of carbon atoms only. Diamond and graphite. Here I have a diamond. It is the hardest substance known. Here we have a little octahedral crystal, as they grow in nature. This came from South Africa. This substance will scratch any substance that we know about. Then there is the other form of carbon - graphite. This is a chunk of natural graphite which is very soft, so soft that my fingernail will scratch it. I can, it is used, as you know, in lead pencils for writing. If I rub this piece of graphite across the paper, it, some of the pieces, some of the bits of graphite tear off and leave their impression there on the paper. Later on, we shall discuss the arrangement of the atoms in diamond and graphite and see how this arrangement explains their properties.

Then, I have here, two crystals. Cleavages, cleavage specimens, from naturally occurring crystals. Salt, sodium chloride, which, when it is hit or cracked with a hammer, it breaks along planes at right angles to one another, And Iceland spar, calcite, CaCO_3 , calcium carbonate, which breaks along planes that are not at right angles to each other. This property of cleavage is determined by the structure of the crystal.

Another interesting example of correlation between structure and properties that we now understand really, essentially, completely, is provided by the silicate minerals. Here I have a natural crystal of feldspar, autocleaved [?] feldspar. The formula of this feldspar is KAlSi_3O_8 . It is a potassium aluminum silicate, aluminosilicate. These other crystals, beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, garnet, $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, tourmaline - I can't remember the

formula of tourmaline right at the moment - silica, quartz, SiO_2 . These substances are hard and strong. They are the principle constituents of the heterogeneous material granite. The pink here is feldspar, the white grains, the white phases are crystals of quartz.

In this case, the atoms are held together by bonds that go in all directions so that the crystals are hard.

Linus Pauling: Another example of a silicate, a silicate with different properties is provided by asbestos. This is a hard rock. It consists, it has nearly the same composition as the feldspar, $\text{Mg}_3\text{Si}_2\text{O}_5\text{OH}_4$. If I take hold of this rock, I can pull it apart into little, minute, very thin fibers. The reason for this, of course, is that the atoms are arranged along long lines, or are bonded along, just to the one axis in the crystal. This is another form of asbestos. It is a form in which there are sheets that are rolled up into minute cylinders that run in this direction, and they are piled so loosely together that they fall apart.

Then there are minerals such as mica. Here I have a specimen of mica. It is pseudo-hexagonal. These are natural faces. It has the black phase present in granite. In mica, the atoms are held together by strong bonds in layers, and these layers are only loosely attached to one another. I might be able, just by using my fingernail, to get hold of a few million of these layers and by pulling to separate them from the rest of the crystal, pull it apart in this way. The layers are strong within the sheet, but they are very loosely superimposed on one another in this crystal.

Now, another example - a metal. Metals have peculiar properties that are characteristic of them. They can be deformed in a special way. They are malleable, which means that they can be hammered out into sheets. They are ductile, which means that they can be drawn out into wires.

Here is a piece of copper, a sheet of copper. I can bend it, and it distorts without breaking. It is tough in this respect; tough and strong. Other metals are still tougher and still stronger - the structural metals. Here are some octahedral crystals, crystals with octahedral-faced development, of native copper; copper as it occurs in nature. We know the structure of the metal copper. It is illustrated by the model over here at the end of the table. Here, each of these spheres represents a copper atom. We know that in a crystal of copper, in the little grains of copper that make up the sheet of the copper metal, or a copper wire, the atoms are arranged in the way that is shown here, a way such that each atom has twelve neighbors. If I look at this atom, I can see that there are six neighbors that surround it in the same plane. Then there are three in contact with it in the plane below and three in the plane above. This way of arranging spheres in space is one of the closest-packed ways. There's no way of getting a given number of spheres into a smaller volume than by arranging them in closest packing. Each copper atom is 2.55 angstrom away from its neighbor. We may say that the effective diameter of the copper atom in copper metal is 2.55 angstrom. One angstrom is a 100 millionth of a centimeter, 10^{-8} centimeters.

This crystal of copper with this structure is a cubic crystal. The octahedron is closely related to the cube, and the tetrahedron, you see here we have a tetrahedron, is also

closely related to the cube. This is the way in which cannonballs are sometimes piled in front of the courthouse on the lawn, in the tetrahedron.

If you are skeptical about the tetrahedron in relation to the cube, I may make a drawing. Here we have a representation of a cube. If I now connect the corners that are not adjacent to one another, I can connect these corners with one another and, in this way, get a drawing of a tetrahedron in a different orientation from this one. Well, I think that I can prove that this has cubic symmetry in a different way. If I start removing copper atoms from this model, I obtain, after awhile, I reach a state where I can lift out a group that have been fastened together and, you see, that here we have fourteen atoms, obviously in a cubic arrangement. There are eight at the corners of the cube, indicated here, and then six others that occupy the centers of the six faces of the cube. The copper crystal has cubic symmetry; each atom is bonded to the twelve surrounding atoms.

Linus Pauling: Well now, the way that chemists have attacked the problem of the relation between the properties of substances and their structure, well, there are various ways. Perhaps the most important way goes back about a hundred years now. It was just a hundred years ago that Frankland, Kekule and Couper, and other people making their contributions, originated the idea of the chemical bond and valence. It was known at that time, a hundred years ago, that substances such as salt, have formulas such as NaCl, hydrogen fluoride is HF, water H₂O; ammonia, NH₃; methane, CH₄.

It was suggested that there are bonds that hold the atoms together; Na to Cl, H to F, water, H to O and another H-O bond, with ammonia, N-H, N-H, N-H, and with methane, C-H, C-H, H, H. Hydrogen and fluorine, sodium and chlorine, are said to be univalent, to have valence one. Water, oxygen is bivalent; it can form two chemical bonds. Nitrogen is trivalent, carbon, is quadrivalent. I have here some models illustrating this; standard ball and stick models. H₂O, NH₃, CH₄.

Many, much of the development of chemistry during the last hundred years has been the result of the development of chemical structure theory. Chemists have learned how to arrange the valence bonds in a drawing, a structural formula of a substance. But it has been found that the problem is really not a completely simple one. The idea of valence in the old-fashioned, rather vague form, has been found to be unsatisfactory and during recent decades, especially in the period beginning about 1916, this concept of valence has been replaced by several more precise concepts. The concept of ionic valence, the concept of covalence, of metallic valence, of some others too that have less general significance. In order to understand these more precise concepts of valence, we have to know something about the electronic structure of atoms.

Let us start out with a discussion of ionic valence. Here we have the periodic system of the elements. The elements are arranged in order of their atomic numbers. Hydrogen, the simplest atom, consists of a nucleus with electric charge plus-one in electronic units, and a single electron outside of the nucleus. Helium has two electrons outside of the nucleus with charge plus-two. Lithium has three electrons outside of a nucleus with charge plus-three and so on. Neon, here, has ten electrons surrounding a nucleus with charge plus-ten.

Now, the electronic structures characteristic of two electrons as in helium, ten electrons as in neon, are especially stable. This is the reason that helium and neon do not form

chemical compounds of the ordinary sort in the way that hydrogen, lithium and other elements form chemical compounds. The third electron on lithium is held only loosely by the atom. It is easy to pull that electron away from the lithium atom. Moreover, fluorine, with nine electrons, has a considerable affinity for an additional electron. It can pick up an electron. The result of this is that if lithium metal and fluorine gas come together, there is a vigorous chemical reaction that leads to the formation of the salt, lithium fluoride.

The structure of lithium fluoride is the following one: lithium has lost one electron, become the lithium ion with the same number of electrons as helium. Fluorine has gained one electron, and become the fluoride ion with the same number of electrons as neon. Then, there is the electrostatic attraction between these ions of opposite electric charge – the same sort of attraction that operates between two pith balls, one of which has a positive charge and one a negative charge – between any two objects that have electric charges of opposite sign. It is this strong electric attraction between the ions, the lithium ion and the fluoride ion, that holds these ions together and the lithium fluoride gas molecule, which you obtain at high temperatures when lithium fluoride is strongly heated, or in the lithium fluoride crystal.

Linus Pauling: We shall start the discussion of the electronic structure of molecules, the electronic interpretation of valence, by discussing the electronic structure of atoms. We know a great deal about the electronic structure of atoms nowadays, and it is the physicists who have determined the information for us. The sort of experimental material that they have used in finding out about electronic structure of atoms is mainly the spectra, the light emitted by atoms, by substances when they are strongly heated or subjected to the action of an electric spark or an electric arc.

The first precise description of an atom, not exactly right, was given by Niels Bohr over forty years ago now. Bohr described the hydrogen atom in its normal state in the following way: He said there is a small, heavy nucleus, the proton, and an electron which moves about it in a circular orbit. The radius of the circular orbit was given by his calculations as 0.530 angstrom and the speed with which it moves in its orbit as 2.18×10^8 centimeters. That is a little less, two-thirds of one percent of the speed of light.

Now, the modern picture of the hydrogen atom in its normal state is somewhat different. We describe the hydrogen atom now as consisting of the same central nucleus, the proton, and the electron, which instead of moving circularly, moves in and out. It is known that the electron does not have angular momentum in its orbit; it is not moving sideways, but only in and out. The average speed, the root-mean square speed with which the electron moves is just the speed that was assigned to the electron by Bohr. And the average distance of the electron from the nucleus is the same as the radius assigned forty years ago by Bohr, to the circular orbit of the Bohr atom.

In addition to this orbit for the normal state of the hydrogen atom, there can be excited states. Bohr talked about a larger circular orbit as representing the first excited state, or an elliptical orbit. According to quantum mechanics, the next most stable orbit for a hydrogen electron and a hydrogen atom, is another one in which the electron moves in and out about the nucleus. The third most stable one is one in which the electron moves

in essentially an elliptical orbit such that there is some sideways motion too, some angular momentum.

The normal state is represented by the symbol $1s$. We talk about the $1s$ orbital. Then the next state by the symbol $2s$ and then the symbol $2p$, and there are three kinds of orbits with the symbol $2p$. We may speak of them, think of them, as having the motion in the plain of the blackboard or in the plain at right angles to the plain of the blackboard this way, or in the third plain, at right angles to both of the other two plains. There is the most stable orbital, the $1s$ orbital, the next most stable, $2s$, and then three $2p$ orbitals. The electron has a spin, as discovered in 1925 by Uhlenbeck and Goudsmit, and this spin of the electron can orient itself in two ways. Either, let's say, with the Earth's magnetic field or against, opposed to the Earth's magnetic field either parallel, or anti-parallel.

The Pauli Exclusion Principle, discovered by Pauli in, I think, 1925 or 1926...Pauli Exclusion Principle states that no two electrons in the universe can be in exactly the same state. If the two electrons are moving around the same nucleus, for example, if we consider a helium atom with a nuclear charge of plus two, there can be one electron in a $1s$ orbital, and then a second in a $1s$ orbital, the same orbital, provided that its spin is opposed, so that one of them has positive spin and one has negative spin. There is a permanent magnetic moment associated with the spin of the electron. We can think of this as corresponding to a small magnet. The spin must be oriented with the North Pole up in the one case for the one electron, and the North Pole down for the other so that the two little magnets neutralize each other's magnetic fields and helium turns out not to have a magnetic moment.

The third electron in an atom such as lithium will have to occupy another orbital. The $1s$ orbital is completely occupied when it has two electrons in it as at helium. This is indicated by putting the superscript 2 on $1s$. $1s^2$ is the symbol for the electron configuration of the helium atom.

Linus Pauling: Now we may discuss the structure of all of the elements, all of the elements that make up the world as we know it in relation to the periodic system of the elements. Let us represent the various elements by showing how their electrons occupy orbitals, and we can plot energy vertically.

We start out with the $1s$ orbital. Hydrogen can have one electron in the $1s$ orbital - I represent it by putting in an arrow pointing upward. Helium can have a second electron - two electrons in the $1s$ orbital. I show them the arrow pointing, pointing down. By Pauli's Principle, that is all the orbitals the electrons that can be placed in the $1s$ orbital.

The next orbital is $2s$. When we come to lithium, the lithium atom with three electrons can have two in the $1s$ orbital, giving a completed helium shell, and then one in $2s$. Beryllium, with atomic number four, and four electrons, can be represented by having two electrons in the $2s$ orbital, its electron configuration is $1s^2, 2s^2$. Then we have the three $2p$ orbitals. They can be occupied successively by electrons in boron, carbon, nitrogen, oxygen, fluorine, neon. At neon, this shell too, is completed - the neon shell.

Now we come to the third shell in the periodic table. The 3s orbital, two 3p orbitals and...that's all that I want now, two 3p orbitals. The succession of elements here, sodium, magnesium, scandium, let me see, silicon, phosphorous, sulfur, chlorine, argon. This succession of eight elements brings us up to the noble gas argon, and we can say that this third shell is the argon shell.

Next, we come to the fourth shell, with atomic number nineteen, potassium. Here we have two electrons, ten electrons, eighteen electrons. These numbers, two, ten, and eighteen, are characteristic of the first three noble gases. With potassium, we have the 4s electrons. With calcium, then, a pair of 4s electrons. Then, the 4p orbitals and the 4d orbitals. One, two, three, four, five of the 4d orbitals. This shell is called the krypton shell, a shell of eighteen electrons occupying nine orbitals...from here, whereas here in the shorter shelves we have only four. These can be occupied by eighteen elements: potassium, calcium, scandium...I think that I said scandium down here, of course, here, I should have said sodium, magnesium, aluminum, silicon, and so on, here we have the first long period of eighteen elements: potassium, calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, germanium, arsenic, selenium, bromine, and krypton. This is, this ends up with krypton and we call it the krypton shell of eighteen elements.

Here, I should mention that the usage of this term "shell" varies somewhat. It has been customary to refer to the k-shell, the l-shell, and the m-shell and so on. Well, the m-shell, in the old designation, is the shell that contains all of the orbitals with the same total quantum number; 3s, 3p and 3d. But, so far as we are concerned, in chemistry, it is more important to lump together the orbitals with roughly the same energy, and here, these are the 4f orbitals, the three 4p orbitals, and the five 3d orbitals.

The next shell, the next shell, is the second, involves the second long period, again of nine orbitals, 5s, 5p, 4d, and eighteen elements ending up with xenon. Xenon, Xe, and this shell of eighteen electrons, nine orbitals, we can call the xenon shell.

The next shell, 6s, then, the 6p orbitals, five 5d orbitals, and seven 4f orbitals comprises the radon shell. This is a very long shell. Sixteen orbitals altogether, thirty-two elements. It brings us up to atomic number, well, let's see, helium has atomic number two, neon, ten, argon, eighteen, krypton, thirty-six, radon, fifty-four. Thirty...no, xenon, 54, radon, eighty-six. Following this comes the second...very long shell 7s, 7p, 6d, 5f, another thirty-two elements that would bring us up to element one hundred eighteen, that we may call eka-radon.

Linus Pauling: We have then, a complete explanation of the periodic system of the elements. The helium shell, one orbital, two elements. Outside of that is the neon shell 3s, 2s orbital, and three 2p orbitals, eight more electrons bringing us up to atomic number ten. Then the argon shell of eight electrons, the krypton shell of eighteen electrons, the xenon shell of eighteen, the radon shell of thirty-two, and, going on to the next shell with thirty-two elements, it would end up at a hundred eighteen.

The elements from titanium, from scandium on to zinc, we may call the transition elements of the iron group. They correspond to putting ten electrons into the five 3d orbitals. Similarly, the elements from deuterium on to cadmium we can call the transition elements of this group. Following lanthanum, there come fourteen elements,

the lanthanons, from cerium to lutetium that correspond to the introduction of fourteen electrons, one at a time, into the seven 4f orbitals.

A great deal is known about the distribution of electrons in the various atoms and ions. This information has been obtained in part by experimental methods and in part by theory, by quantum mechanical theory. The results of x-ray experiments and electron diffraction experiments have shown that the electron distributions agree well with those that have been calculated by theoretical physicists using the Schrödinger wave equation, the fundamental equation in quantum mechanics.

I have some drawings that I made, in fact, twenty-four years ago, when I was going to give a lecture in Santa Barbara, some drawings that show how the electrons are distributed in the various ions. I, I don't remember just why I was so interested in ions at that time, but I made the drawings for, for example, the bromide ion, a bromine atom that has picked up an extra electron, and for the rubidium ion, a rubidium atom that has lost one electron. These drawings are a good representation, I believe, pretty accurate rough representations, of the electron distributions in the various ions.

Here, I have the drawing of lithium. The nucleus at the center, the lithium ion, Li^+ , the nucleus at the center, and then two electrons constituting a completed helium shell that moves in and out and have a distribution in space that is indicated by this drawing.

As we go on across the periodic table, from lithium towards the end of the first short group, we come to the fluorine atom which, being just short of neon, can pick up one additional electron. The electron, electronic structure of the fluoride ion is shown here. The nucleus, two electrons close in to the nucleus that constitute the helium shell, shrunk in because the nuclear charge is large, much larger than for lithium, and then eight electrons in this fluoride ion, two of which are moving in and out radially, the other six in somewhat elliptical orbits with the electron distribution shown here. You see that the fluoride ion is several times larger, roughly three times the diameter of the lithium ion.

Then here is the sodium ion. Sodium ion, sodium has eleven electrons. One of them has been lost to form the sodium ion, Na^+ , leaving ten electrons just as in the fluoride ion. These ten electrons are arranged, are distributed as shown here. The two in the helium shell are close in, the eight that constitute the neon shell are also shrunk in somewhat from the dimensions in the fluoride ion. This is the effect of the increase by about twenty percent in effective nuclear charge on going from fluorine to sodium. The scale is shown here, one angstrom. The sodium ion is about one angstrom in radius. The conventional crystal radius for sodium ion is 0.95 angstrom.

From sodium we continue across the first short period of the Periodic Table to chlorine, which is just one short of argon. The chlorine atom picks up an electron easily to form the chloride ion and the structure of the chloride ion is as indicated here. Two electrons in the k shell, the helium shell, then eight in the neon shell, and eight more in the argon shell, giving the ion with one negative charge.

Linus Pauling: Here, I have the next alkali metal ion, the cation potassium, charge of nineteen, one electron missing from it, the outermost electron beyond the argon shell is easily removed, leaves it with eighteen electrons and a positive charge. The electronic

structure is almost identical with that of the chloride ion. The two innermost electrons have shrunk in a bit, the eight electrons, the eight electrons of the neon shell have shrunk a bit, and the eight electrons of the argon shell have shrunk in a bit. It is evident that we would expect the radius, the effective radius, the effective size of the potassium ion, to be somewhat less than that of the chloride ion. Their dimensions are, potassium, I think, 1.33 angstrom, chlorine, 1.81 angstrom.

Now we move on to bromide ion, atomic number 35, 36 electrons, two in the helium shell, eight in the neon shell, eight in the argon shell, and eighteen in the krypton shell. Rubidium is the iso-electronic ion, 37 is its atomic number, it has lost one electron, the thirty-six electrons are arranged in the same shells; two in helium, eight in neon, eight in argon, eighteen in the krypton shell, and the ion has shrunk in size compared with the bromide ion.

The element iodine, with atomic number fifty-three, is just one short of xenon. It can pick up one electron, getting fifty-four electrons, and its electronic structure is as shown here: two k electrons very close in to the nucleus, then eight electrons in the argon-, in the neon shell, eight in the argon shell, eighteen in the krypton shell, and eighteen in the xenon shell. Iodine, the iodide ion, is somewhat larger than the bromide ion, which is somewhat larger than the chloride ion and so on.

Cesium loses one of its fifty-five electrons easily to assume the electronic structure of xenon. It has two k electrons, eight in the neon shell, eight in the argon shell, eight in the krypton shell, and eight in the xenon shell. The sizes of ions, the sizes of these alkali ions and halogenide ions, and also the sizes of the other ions, beryllium, double-plus magnesium, double-plus scandium, or calcium, double-plus strontium, double-plus barium, double-plus and so on, are of much value in the discussion of the properties of substances.

Sodium chloride, when heated very strongly, forms diatomic gas molecules, NaCl. It also forms some more complicated molecules, Na₂Cl₂ and so on. These easily can condense to form sodium chloride crystals. The structure of the sodium chloride crystal is indicated by this model. This model is about on the scale of one inch to one angstrom, linear magnification two hundred and fifty million fold, so that it isn't a very good representation of the big crystal of sodium chloride that we have, that we saw earlier in this lecture. If we wanted to make this model represent the structure of sodium, of the crystal of sodium chloride, this one, we would have to continue it on until it was about three times the diameter of the Earth. That is, its volume would be about twenty-seven times that of the Earth if the atoms were this big.

Well, here we have the chloride ion and the sodium ion on the scale corresponding to their relative electron distributions; 1.81 angstroms for the radius of chlorine and about 0.95 angstrom for the radius of sodium. They are arranged in this way in the sodium chloride crystal. Each sodium ion is surrounded by an octahedron of six chloride ions, and each chloride ion is surrounded by an octahedron, four here, one behind and one in front, of six sodium ions. The ligancy, or coordination number, of the sodium ion is six in this structure.

It is easy to understand why sodium chloride has a cubic cleavage. You see, here in this front face, there are nine, ten, eleven, thirteen of these chloride ions and twelve sodium

ions, but if it were a bigger face, there would be exactly the same number of sodium ions and chloride ions so that this layer of the crystal would be electrically neutral. We could expect then, that it might be possible to split off the electrically neutral layer and in this way achieve the cubic cleavage of the crystal. On the other hand, if we cut along this diagonal, perpendicular to the body diagonal of the cube, we have first a layer of chloride ions with negative charge, then a layer of sodium ions with positive charge, then a layer of negative ions with chloride, with, of chloride ions with negative charge, which would be hard to separate the successive charged layers from one another.

Linus Pauling: Many properties of substances can be discussed in terms of the sizes of the ions. One example is the formula of hydrates. Sodium chloride doesn't form hydrates ordinarily, out of aqueous solutions, salt crystallizes as anhydrous NaCl. The attraction of the sodium ion and chloride ion for water molecules is not very great. But the ions with larger electric charge, the bivalent ions, beryllium, magnesium, calcium, usually crystallize out of aqueous, their salts crystallize with water of crystallization, and the water of crystallization is, to some extent, predictable. For example, beryllium is a small ion, magnesium is a larger ion.

The size of magnesium relative to the size of a water molecule is about the same as sodium relative to chlorine. We would expect then that a magnesium ion would coordinate six water molecules, about itself at the corners of an octahedron and, in fact, magnesium chloride crystallizes with formula $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Many of the salts of magnesium appear as crystallized from aqueous solution with six molecules of water which, without doubt, in fact, we know from x-ray diffraction experiment, are arranged octahedrally about the magnesium ion.

The beryllium ion is smaller, so small that it can fit inside a tetrahedron of four water molecules arranged in this way, and beryllium sulfate crystallizes as $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, the four water molecules being arranged in this tetrahedral manner around the beryllium ion.

In addition to the metals that are close to the noble gases in the Periodic Table - lithium and beryllium close to helium, sodium and magnesium close to neon, and so on - and that easily lose one or two or three electrons to become positive ions, there are also a number of other metals, those in the transition groups that easily lose electrons to become cations. For example, chromium, manganese, iron, cobalt, nickel, copper, zinc appear in most of their compounds as cations with charge plus two or plus three. Zinc, in the period 2b of the Periodic Table, zinc forms the ion Zn^{++} , Zn double plus. With atomic number thirty, it loses two electrons easily to form the zinc ion which has twenty-eight electrons. Now, eighteen of these twenty-eight electrons are in the shells up to argon, completed argon structure, ten more occupy, ten more are present in the krypton shell. They are just enough to occupy the five orbitals of the 3d sub shell.

Copper, when it loses one electron, to form the cuprous ion, has also achieved to be the structure in which there are ten electrons in the five 3d orbitals. But of course, this state, this state with valency one, charge plus one, is not the most stable one for copper. Most copper salts such as copper sulfate, blue vitriol, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, most copper salts involve copper that has lost two electrons and there is no simple explanation of the tendency of copper to lost two electrons.

The most that we can say for these metals in the transition series is that they lose one electron easily. The second electron is pulled off with greater difficulty because one is removing an electron from an ion that already has a positive charge that is pulling the electron back and sometimes it is possible also to remove a third electron. These elements in the transition periods usually turn up with ions that have charge plus two or plus three. And, although it is possible to get some sort of understanding of why one, understanding of why one charge plus two or plus three is the more stable for nickel, say, and another, the more stable for cobalt. This is not a simple branch of chemical theory.

Linus Pauling: This sort of valence, we can say that there is a chemical bond connecting the sodium ion with the six chloride ions that surround it in this crystal. This sort of valence is, I think, very well understood. The sodium ion here has a single positive charge. It is not attached to a chloride ion to form a sodium chloride molecule in the crystal. It is similarly related to all six of the chloride ions that surround it. I think that it is sensible to say that there is a one-sixth bond. One-sixth of an ionic bond between each sodium ion and each of the six chloride ions around it. And that the chloride ions itself with charge minus-one has its charge satisfied by the six one-sixth bonds that come to it from the six sodium ions that surround it.

Many substances can be discussed satisfactorily in terms of the ionic bond with transfer of electrons from one atom to another. On the other hand, there are many substances that can't be discussed in this way. For example, the hydrogen molecule, H_2 . Neither hydrogen atom picks up an electron from the other. Instead, the molecule has the structure shown here. The two electrons are held jointly by the two atoms; they constitute the bond between the two atoms. To form this sort of bond, the covalent bond, the bond that Professor G. N. Lewis of Berkeley called the chemical bond, we need to have an orbital for each of the two atoms and a pair of electrons.

During the next hour, we shall talk about the covalent bond and the structure of molecules containing bonds of this sort

Linus Pauling: In this lecture, the second of our series on valence and the electronic structure of atoms, molecules and crystals, I shall talk about the covalent bond and the shared electron pair bond – they are the same thing, two different names.

The covalent bond; covalent, covalence is an aspect of valence that I think comes closer to the old-fashioned, rather vague concept of valence than do the other, more precise aspects of valence that we make use of at the present time.

The theory of structural chemistry involving the idea of the covalent bond represented by a line drawn between two symbols, the symbols for two atoms, this theory is one of the greatest constructs of the human mind that has ever been formulated, perhaps the greatest of all. The theory of structure, of structural chemistry, has been, was developed about a hundred years ago. It was in 1852 that Frankland suggested that different elements have different combining powers, can combine with different numbers of atoms of other elements. In 1858, Couper and Kekule invented the idea of the chemical bond and discovered the quadrivalence of carbon. Then, there were, there was great progress in chemistry with the aid of this relatively simple theory that had been obtained by induction from the many thousands of facts of chemistry. It was possible for

chemists to make the extraordinary progress that has led to modern technology and medicine. The structure theory assisted the imagination of man in such a way that he was able to make discoveries that would not have been made otherwise.

I should like to start out by talking about the simple structure theory, the simple idea of the chemical bond in the substances that we now consider to contain covalent bonds. The...as an example, I may take methane, represented by this model, a carbon atom with four hydrogen atoms attached. The right orbit, the formula C, H, H, H, H. And of course, Couper and Kekule recognized that the carbon atoms forming four bonds can also be attached to one another.

I have another model, here, representing the structure of ethane, the next hydrocarbon in the aliphatic series, C_2H_6 , two carbon atoms attached together, six hydrogen atoms. Each carbon atom is quadrivalent, forms four bonds, one with the other carbon atom and three with the three hydrogen atoms that in the structural formula are shown connected to it by the valence bonds.

As a more complicated example, I may show ethanol, ethyl alcohol. Here we have the two carbon atoms bonded together, three hydrogen atoms, two here, a bond to the oxygen atom, and then a bond to the hydrogen atom on oxygen. C_2H_5OH , ethanol.

I may mention that these ball and stick models are quite illuminating but they do not give a really correct idea of the shape of the molecule. The ethanol molecule does not have a thin portion that connects the carbon atom to the hydrogen atom. Instead, the electron distribution in space is more satisfactorily represented by this model, a space-filling model in which the atoms are drawn, are shown as spheres with a radius that corresponds approximately to the contact, effective contact radius, when the molecules are piled together in a liquid or a crystal. If there were another molecule in solution, say in ethanol, for example this rather larger molecule, then the molecules would roll over one another in such a way that they do, would not get closer, much closer to one another than the distance corresponding to contact between the spheres that represent the atoms in these models.

Linus Pauling: A very important contribution to structure theory was made in 1874 by the Dutch chemist van't Hoff and the French chemist, Le Bel independently of one another. This is the idea that the four bonds formed by the carbon atom are not directed out toward the corners of the square in one plane as indicated here on the blackboard, or are not so loose-jointed that they have no well defined direction, but instead are directed toward the four corners of a tetrahedron.

All of our models are built in this way. Here we have the methane molecule with the four bonds shown proceeding toward the four corners of a tetrahedron, a regular tetrahedron. This has been found in recent years by the determination of the structures of crystals and of gas molecules, by the x-ray diffraction method, the electron diffraction method, and various spectroscopic methods, that the angles between single bonds formed by a carbon atom remain in all substances quite close to the tetrahedral angle, the angle for a regular tetrahedron, a hundred nine degrees, twenty-eight minutes.

The tetrahedral carbon atom is a very important part of chemistry. I think that the discovery of the tetrahedral carbon atom was a wonderful thing – it shows the power of

man's mind. The facts were that in 1874, it was known as a result of the work of Pasteur that some substances can form crystals that have either a left-handed appearance or a right-handed appearance.

Van't Hoff and Le Bel asked how is it possible for substances to be built up of molecules that are right-handed or left-handed? Two different kinds of molecules that are related to one another in the way that the right hand and the left hand are related. They showed that the tetrahedral carbon atom provides the explanation of these facts, that the four bonds of a carbon atom are connected to four different kinds of atoms or groups.

For example, a hydrogen atom, a methyl group CH_3 , a chlorine atom, a bromine atom. Then, this tetrahedral molecule can be either a right-handed molecule or a left-handed molecule and the right-handed molecule does not become left-handed by any translational or rotational motion in space. Only by breaking the bond and moving it around to the other side can you convert the right-handed molecule into the left-handed molecule. Recent investigations, recent structure determinations, have of course, completely verified this idea of the tetrahedral carbon atom.

Linus Pauling: The simple chemical structure theory permits one to understand the existence of isomers. I have here a model. Let me start with this one. I have here a model representing one of the two forms of butane, C_4H_{10} , 3, 6, 7, 8, 9, 10, C_4H_{10} . This is normal butane, a straight chain hydrocarbon. It is called a straight chain even though the bonds are at the tetrahedral angle here so that the chain is a zigzag chain.

Normal butane is one substance. There is another substance with formula C_4H_{10} that has somewhat different properties. This other substance, called isobutane, is represented by this model. Here we have again four carbon atoms and 3, 6, 9, 10, ten hydrogen atoms, but the bonding between atoms is different for isobutane from that of normal butane.

These are the only two ways in which four carbon atoms and ten hydrogen atoms can be attached together with each carbon atom forming four bonds and each hydrogen atom one. And, corresponding to this, there are only two isomers known, two substances known, that have the composition C_4H_{10} . This provides an interesting, simple example of the power of chemical structure theory.

Now, there are many other sorts of molecules that one can build that are compatible with the simple principles of structure theory. I have here a model of a new sort in which there is a ring, a cycle, of carbon atoms. This molecule is the molecule of cyclopentane, C_5H_{10} . The angle in a pentagon is a hundred and eight degrees, so very close to the tetrahedral angle so that there is practically no strain in this molecule.

On the other hand, a smaller ring involves some strain. No longer are we able to use half-inch wood dowel rods in representing the bond. We have to have strings in this model which represents cyclopropane, C_3H_6 . Here we have bent bonds connecting the carbon atoms. If the bonds came directly from carbon atom to carbon atom, the angle would be sixty degrees instead of the tetrahedral angle, a hundred and nine degrees, twenty-eight minutes. We can represent the structure by the use of these bent bonds. There is some strain associated with the bent bonds so that cyclopropane is somewhat

less stable than one would expect from a molecule with the same composition and without the bent bonds.

It is interesting that this substance, cyclopropane, is used as a general anesthetic. It produces anesthesia. I think this is an illustration of the present situation in physiology, biochemistry, our lack of understanding of the nature of the human body. Why is it that this particular molecule produces anesthesia? Why is it that chloroform, CHCl_3 , produces anesthesia? Nobody really knows the answer. No one is able to predict what substances will be anesthetics and what not. Here we have chloroform with a hydrogen atom down here - I'll hide this chlorine atom to make it into chloroform. No one knows why chloroform serves as an anesthetic too.

Some light on this question is provided by the fact that xenon is also a general anesthetic. Now, xenon is one of the noble gases, atomic number fifty-four. It forms no chemical compounds in which it forms chemical bonds. It will, in fact, form a hydrate, xenon hydrate, in which the water molecules are arranged together, attached to one another in such a way as to make cages, little rooms, in which the xenon atoms fit. It is interesting that cyclopropane forms a similar hydrate, and chloroform forms a similar hydrate. In the case of chloroform, the hydrate is something like $\text{CHCl}_3 \cdot 17\text{H}_2\text{O}$.

I think that it may well be that the effect of these substances in producing general anesthesia is related to their power to form moderately stable hydrates, stable at temperatures ten degrees or more above the freezing point of water. Perhaps somewhere in the tissues in the nervous system, there are little regions where the water is tied down into a sort of pseudo-crystalline aggregate by the molecules of the general anesthetic and the normal metabolic activities of the nervous system are not able then to go on. But we really don't know enough about the chemistry of the human body to be able to give an explanation of this.

Linus Pauling: Well, let me go on to discuss some things that we do know about. This model. This model represents the structure of ethylene. It has something new in it; a new structural feature. Here we have two bonds connecting one carbon atom with another carbon atom. A double bond represented in a conventional way by two lines between the carbon atoms.

Ethylene is an interesting substance. It causes oranges to ripen. If you have oranges that aren't very ripe, look sort of yellow in the freight car and put some ethylene into the freight car, the oranges develop a beautiful orange color. Nobody knows why that goes on either.

Well here is a double bond, we can say two bent bonds holding the carbon atoms together. Now, if this double bond is described as involving two tetrahedra, two tetrahedra that are attached together with one edge in common, then we can see that there is restriction in the rotation. It is not possible to twist the molecule around, through, one end through a hundred and eighty degrees relative to the other end. To do that, one would have to break a bond, and this takes a lot of energy.

The result of this is that a new sort of isomer is found in substituted ethylenes. If we replace one of the hydrogen atoms on this end of the molecule with say a chlorine atom, and one on the other end with a chlorine atom, we may do this in either one of two

ways. This hydrogen and this hydrogen may be replaced with chlorine. That gives one substance. Or this hydrogen and the opposite hydrogen may be replaced. That gives another substance. These substances have different properties, different chemical and physical properties. They are represented by the model shown here. This is called cis-dichloroethylene, in which the two chlorine atoms are on the same side of the double bond. This molecule, represented by this model, is called trans-dichloroethylene in which the two chlorine atoms are on opposite sides of the double bond.

Well, here again, we have only two isomers with the formula $C_2H_2Cl_2$ and with the chlorine atoms on separate carbon atoms. There is also a third isomer in which there are two hydrogen atoms attached to one carbon atom, two chlorine atoms attached to the other carbon atom.

In addition to the double bond, the triple bond is known. There are substances, such as acetylene, that contain a carbon-carbon triple bond. Here we have three bent bondsholding the two carbon atoms together. The other two bonds project out in opposite directions. The molecule acetylene, C_2H_2 , is a linear molecule. The conventional representation of this molecule is C, H, C, H.

No quadruple bond is known. Nobody has ever recognized the quadruple bond, at least so far as I am aware. In reading the chemical literature, I have never seen mention of evidence that a quadruple bond exists. Perhaps we can understand that, too, in terms of the tetrahedral carbon atom. For carbon, any rate, the four bonds come out in these directions. We can have a double bond by bending the bond, triple bond by sharing two faces of the two tetrahedra and bending the bounds about enough, but the fourth bond would have to make a terrific bend in order to get around from the backside of this carbon atom to the backside of the other carbon atom.

Linus Pauling: Now, let us discuss the modern aspects of valence theory, structure theory. First, let me say that the classical structure theory, the older structure theory, has not been discarded. There has not been a revolution of such a nature that the old has been thrown out and the new has come in. Classical structure theory is still valid. There have been some improvements in structure theory, some problems of molecular structure and valence that were hard to discuss, hard to understand before, can now be discussed in a reasonable and sensible way because of the additions that have been made. Ideas about hybridized bond orbitals, about the theory of resonance, partial ionic character of covalent bonds have come in and have made chemical structure theory more powerful.

The whole theory, classical structure theory and modern structure theory, have a sound base in experiment. It has, it has been developed largely by induction from the tens of thousands of chemical facts with, in the case of the modern development, a little help, or considerable help, I should say, from ideas that have been suggested by the theory of quantum mechanics for which we are indebted to the physicists.

The modern theory began in 1916 when Professor Lewis introduced the idea of the shared electron pair chemical bond and much contribution was made, also, by Irving Langmuir. The principle...statements that we can make about a chemical bond now are that in order to form a chemical bond between two atoms, you need to have an orbital for each atom. Let's say atom A must have an orbital, atom B must have an orbital, and

two electrons are involved, which I may write in this way, and their spins must be opposed. One orbital for each of the two atoms and a pair of electrons with opposed spins, which serve to hold the atoms together.

Here, I have a drawing representing the structure of the hydrogen molecule, H_2 . The two nuclei, the two protons, are at these positions, seventy-four hundredths of an angstrom apart, and the two electrons are distributed in space roughly as shown here, with a good concentration right in the region between the two nuclei. It is almost as if the nuclei were ball bearings, steel ball bearings around which some rubber has been vulcanized to hold these ball bearings firmly at this distance apart, does not permit them to escape from one another. This is the standard Lewis symbol for the hydrogen molecule, H_2 . The two electrons are shown between the symbols for the two hydrogen atoms.

We see that we can say that each of the hydrogen atoms has succeeded in obtaining the helium structure. This orbital for hydrogen, the 1s orbital, is occupied by the pair of electrons, which is, also occupies the 1s orbital for the other hydrogen atom.

The idea that you must have a stable orbital for each atom in order to form a bond and a pair of electrons permits a considerable addition to the power of chemical structure theory. Here, I have a drawing representing the electronic structure of the water molecule. The water molecule, H_2O , has the Lewis symbol as shown here. The pair of electrons in the helium shell for oxygen is not indicated, only those in the neon shell. Here is an unshared pair of electrons occupying one orbital, a second unshared pair occupying a second orbital, a third shared pair, in this case, occupying the third orbital, and a shared pair occupying the fourth orbital. The oxygen atom now has four electron pairs, eight electrons in its neon shell. It has achieved the structure of the neon atom by sharing electrons, and the hydrogen atoms, as before, using their 1s orbitals, have achieved the helium configuration.

Many structures, many molecules, have structures such that each atom achieves the electronic structure of the nearest noble gas with two, ten, eighteen, thirty-six, fifty-four, and so on, electrons. The oxygen-hydrogen distance is known. 0.965 angstroms, the angle between the oxygen atoms is known experimentally, a hundred and four degrees, thirty minutes.

These distances are interesting in that they, the distances, as determined by spectroscopic or diffraction measurements, in that they give us an idea about the significance of the chemical bond. The carbon-carbon distance, well, let me look at this, the chlorine-chlorine distance, in the chlorine molecule, Cl_2 , is 1.98 angstrom. We can write the Lewis formula Cl, Cl , and I shall show also the electrons in the valence shell, the argon shell of each chlorine atom. I have written here a line like this to represent the two electrons that are shared between the chlorine atoms.

Chlorine has only sixteen electrons, that is seven in the argon shell, but by sharing a pair each chlorine atom succeeds in achieving the argon structure with eighteen electrons. The distance between the two chlorine atoms is 1.98 angstrom, as determined spectroscopically and by electron diffraction. The distance between the two carbon atoms in ethane, the carbon-carbon distance in ethane...I'll change this to ethane, CH_3 , is 1.54 angstrom. 1.54 angstrom.

Now, when we examine carbon tetrachloride, by spectroscopic methods or electron diffraction, we find that the carbon-chlorine distance in carbon tetrachloride, is 1.76 angstrom. Carbon, four bonds to chlorine, I might as well continue to give the example. Well, for this chlorine atom, here again, by forming the bond, chlorine has achieved the argon structure and the carbon atom has achieved the neon structure. This distance is found to be 1.76 angstrom. 1.76 angstrom, 1.98 angstrom in chlorine, plus 1.54 angstrom in ethane, that is two, 3.52, half of that is 1.76. So, the carbon-carbon bond has a length just midway between the lengths of the carbon, the carbon-chlorine bond has a length just midway between the lengths of the carbon-carbon single bonds in ethane, and the carbon, chlorine-chlorine bonds in the chlorine molecule.

Linus Pauling: While I'm on the subject, I might mention diamond. Here is a model not built on such a large scale, so, small enough so that I'm able to lift it. A model of diamond. Each carbon atom is attached by carbon-carbon single bonds. Two, four others that surround this tetrahedrally. And, the distance found experimentally between the carbon atoms is 1.54 angstrom, just the distance that is found in ethane, and in many other substances in which there are carbon-carbon single bonds.

We can understand too why diamond is so hard. Here are these chemical bonds, strong bonds, which connect all of the atoms in the crystal together into a single molecule. In order to break a crystal of diamond, as for example if you tried to scratch it with some other substance, it would be necessary to carry out a chemical reaction, the reaction of breaking carbon-carbon bonds. This is so hard to do, the bonds are so strong, that the substance is very hard, the hardest substance known. I may mention, also, that the double bond, which is the stronger bond, has length 1.33 angstrom, the triple bond, still stronger, has length 1.20 angstrom. As the bond between the carbon atoms gets stronger, the atoms are pulled more and more closely together.

There is one aspect of the carbon atom, the bonds formed by the carbon atom that I should mention. The question is this: You remember that the orbitals for the carbon atom are the 1s orbital, the 2s orbital, and the 3 2p orbitals. Now, these are the orbitals in the valence shell, and one might well ask 'is not one bond formed by the carbon atom not different from the other three?' The answer to this is a simple one. No, the four bonds are equivalent. And, we can describe these bonds in terms of four equivalent orbitals. Instead of the s orbitals and the p orbitals, we can formulate, as hybrid orbitals, four that are directed toward the four corners of a regular tetrahedron, and these orbitals are perfectly satisfactory in providing an explanation of the four equivalent tetrahedral bonds.

I think that it is interesting that if it had happened, as it might well have happened, that chemists discovered quantum theory, wave mechanics, rather than the physicists, then we would be saying that the s orbital and the p orbital that the chemists are interested in, are hybrid orbitals, formed of the four equivalent tetrahedral orbitals of the carbon atom.

Let us consider now some substances, some molecules, for which the classical valence theory was not satisfactory. An example is benzene, the benzene molecule C_6H_6 , may be represented, according to classical theory, by this structure, a six-membered carbon ring. In order that the carbon atom be quadrivalent, we must have, we must have in this six-membered carbon ring, not only the bonds from carbon to hydrogen and carbon to carbon, but also double bonds.

But, chemists found a hundred years ago that, if two of these hydrogen atoms were replaced by, say, chlorine atoms, one did not obtain two substances, a substance in which the chlorine atoms were around carbon atoms held together by a single bond, and another substance in which chlorine atoms surround carbon atoms held together by a double bond, instead, only one substance could be obtained of this sort.

The explanation of this is given by the theory of resonance. This theory states that sometimes, instead of writing a single valence bond structure to represent a molecule, one must write two or more valence bond structures and lump them together. Benzene is described now as being a resonance hybrid of these two, those are identical. I'll have to draw the double bonds differently. There's the second one, with the chlorine atoms here for dichlorobenzene. We write these two Kekule structures, a single structure of this sort was first written by Kekule nearly a hundred years ago. We write these two Kekule structures and say that the two structures together provide a satisfactory description of the benzene molecule.

A similar sort of structure can be written for graphite. This represents a portion of the graphite crystal. A very soft substance, the molecule is to be thought of as being infinite in size, a very large layer consisting of hexagonal rings. If I start to represent this structure, I can show carbon atoms attached together in rings. Now, I need to have a double bond on this carbon atom in order that there will be a quadrivalent carbon atom. But, the double bond does not to be here. It may be there or here or here. There are a great many structures that I can draw to represent the molecule of graphite.

The physical properties of graphite I nicely explained by this structure. On this scale, a scale of this model, the layers, these giant two dimensional molecules, are about this far away from one another and very loosely attached to one another so that they can slide back and forth relative to one another.

Linus Pauling: There are many other substances for which a satisfactory structure cannot be written, a single satisfactory structure and instead two or more, two or more structures must be written.

Ozone is an example. The ozone molecule consists of three oxygen atoms with about a hundred and twenty degree angle in this region. If we try to assign a structure in which each of the stable orbitals, too many there, each of the stable orbitals is used in forming a bond or for occupancy by unshared pairs, then we find that this is the best that we can do. Each oxygen atom has now achieved the neon structure: two unshared pairs and two shared pairs, three unshared pairs and one shared pair, one unshared pair and three shared pairs. But, this makes this oxygen-oxygen bond different from this, whereas it is known that these oxygen-oxygen bonds are equivalent.

The solution to this difficulty is that there is another way of introducing the valence bonds in which the single bond and the double bond have changed places. Ozone has a resonating structure. Each of these bonds can be described as being a hybrid of a single bond and a double bond, a bond with about one and a half bond character.

This is a model, a small model, showing the correct packing dimensions of the atoms of sulfur dioxide. The two oxygen atoms attach to sulfur, the bond angle again about a hundred twenty degrees. And, here again, there's a double bond and a single bond with

resonance between the two structures, double bond, single bond and double bond, single bond.

The criticism has been made, rather often, of the theory of resonance, that it is artificial. It is said, for example, that nobody has ever found a benzene, nobody has ever synthesized benzene that has one Kekule structure, and that accordingly, one should not talk about the first Kekule structure and the second Kekule structure.

Now, the fact is that the theory of resonance is no more artificial than ordinary structure theory. It is true that nobody has ever succeeded in bringing into the laboratory, a flask full, a beaker full of benzene with the first Kekule structure, and another beaker full of benzene with the second Kekule structure. But in fact, nobody has ever succeeded in bringing into the laboratory a beaker full of carbon-carbon single bonds or carbon-carbon double bonds or carbon-hydrogen bonds, and yet we are happy to talk about the carbon-hydrogen single bonds, the carbon-carbon double bonds, as structural features of molecules, of the ethylene molecule, the methane molecule, the ethane molecule.

In fact, of course, every molecule is something of its own. No two molecules are exactly alike. The carbon-carbon distance in one molecule, the average carbon-carbon distance is a little different from the carbon-carbon distance in another molecule. In isobutane, the carbon-carbon distance may differ by a few thousandths of an angstrom from that in ethane. Yet, the approximation of the carbon-carbon distance to the standard value 1.54 is very good for many substances, the carbon-hydrogen distance often has a standard value of about 1.08 angstrom.

And we have found it, chemists have found it, very useful to make, to talk about structures for molecules that involve the idea of the carbon-carbon single bond and the carbon-carbon double bond, even though these are constructs of the intellect, rather than a part of nature that can be completely isolated.

Well, in the same way, it is found very useful to talk about the resonance of the ozone molecule between this valence bond structure and this valence bond structure or to speak of ozone as a hybrid that has a structure that can be represented by two different valence bond structures

Linus Pauling: There is another question that we can answer with use of the theory of resonance and in answering it, we achieve a great simplification of chemistry, coordination of a great number of facts of inorganic chemistry.

I may use hydrogen chloride as an example in discussing this question. What is the structure of hydrogen chloride, HCl? Well, I can write its Lewis structure in this way. There's a bond, a covalent bond, between hydrogen and chlorine. Hydrogen has achieved the helium structure, chlorine the argon structure. But of course, if I were giving the talk on ionic valence, I might say I'll write $H^+ Cl^-$. And thirty years ago, there was much argument as to which of these structure, the ionic structure, or the covalent structure was the correct one.

Well, we know the answer now. The theory of resonance [unintelligible] can be written for hydrogen chloride. A normal covalent structure, similar to the structure in the

hydrogen molecule and the structure in the chlorine molecule, intermediate between these structures, and an ionic structure, with chlorine negative and hydrogen positive.

Well, now we may ask, how, to what extent do these two structures contribute? And there are several ways of getting an answer to this. In the hydrogen chloride molecule, the distance between the nuclei is 1.27 angstrom. The electric dipole moment of HCl is known. It corresponds to a charge plus 0.2 on hydrogen and minus 0.2 on chlorine. We can say, then, that there is about twenty percent ionic character and eighty percent covalent character to the hydrogen chloride molecule.

In fact, in fact, it is possible to correlate the amount of ionic character of molecules containing single bonds, with a scale, an electronegativity scale, starting with fluorine, 4.0, oxygen, 3.5, nitrogen, 3.0, carbon, 2.5, hydrogen, 2.1, boron, 2.0, beryllium, 1.5, lithium, 1.0, chlorine, 3.0, sulfur, 2.5, bromine, 2.8, iodine, 2.4. And, the amount of partial ionic character depends upon how far apart the elements are in this electronegativity scale.

You see, this is a sort of skewed Periodic Table. Instead, the halogens, instead of following the line directly below the one, are skewed over in this way. The most electronegative element is fluorine, the next most electronegative element oxygen, and so on across. Now, elements, differ in electronegativity by about one unit. Chlorine and hydrogen, 0.9. Then, there is about twenty percent partial ionic character. If they differ in electronegativity by about two units, the partial ionic character is more than fifty percent, some sixty or seventy percent.

This electronegativity scale was set up from the consideration that whenever there is resonance between two structures, a substance is stabilized. Benzene is much more stable than an ordinary unsaturated compound involving a double bond. It is the resonance energy between the two Kekule structures that provides the extra stabilization.

Hydrogen chloride is more stable than it would be if it had a normal covalent structure. H_2 plus Cl_2 forms $2HCl$ with the liberation of 2×22 kilocalories per mol of energy. The bond, HCl bond, this twenty-two kilocalories per mol, per mol more stable than the average of the H-H bond and the Cl-Cl bond. Hydrogen and fluorine, H_2 plus F_2 form $2HF$ with 2×64 kilocalories per mol. Hydrogen and bromine form $2HBr$ with 2×12 . Hydrogen and iodine form $2HI$ with 2×2 kilocalories per mol. Very nearly zero.

Now, iodine, 2.4, and hydrogen, 2.1, have nearly the same electronegativity. Consequently, the HI bond is almost a normal covalent bond, very little partial ionic character, and correspondingly, the bond is hardly anymore stable than the average of the bond for a hydrogen molecule and an iodine molecule.

Bromine is somewhat more electronegative than hydrogen, 2.8 against 2.1, and the bond is twelve kilocalories per mol more stable. Chlorine is still more electronegative, difference of 0.9, the bond is twenty-two kilocalories per mol more stable. For fluorine, sixty-four kilocalories per mol more stable

As a rough approximation, we can say that the partial ionic character of a bond is equal to the amount of extra stability of the bond, as given by the heat of formation of the

substance in kilocalories per mol. About two percent partial ionic character in HI, twelve percent in HBr, twenty-two percent in HCl, sixty-four percent in HF.

Now, knowing the electronegativities of elements, we can make predictions about the heats of formation of all substances that involve single bonds. I can take, for example, graphite and hydrogen to form methane. What would be the heat of the reaction? Graphite plus hydrogen to form methane. Carbon, 2.5, hydrogen, 2.1, the bond corresponds to about four tenths difference. I know by comparison with HI and HBr, there will be somewhere around five kilocalories per mol extra stability of the hydrogen-carbon bond, and for a methane molecule with four of these bonds then, about twenty kilocalories per mol as the heat of formation of the molecule.

Linus Pauling: There are many other properties of substances that can be discussed in a straightforward way on the basis of the electronegativities of the atoms and the partial ionic character of the bonds. The relation between the energy that is liberated and the difference, or when a bond between two atoms is formed, and the difference in electronegativity of the atoms is the following: The extra energy, resonance energy, due to the partial ionic character of a covalent bond is approximately equal to twenty-five kilocalories per mol, twenty-five kilocalories per mol times the square of the difference in the electronegativities of the two atoms. I can write $X_a - X_b$ where X represents the electronegativity. X_a is the electronegativity of atom A while X_b is the electronegativity of atom B. The difference, squared, multiplied by twenty-five kilocalories per mol, gives the heat of formation of the bond and multiplied by twenty-five percent, gives the partial ionic character of the bond.

This explanation of the heat of reactions, all sorts of reactions, applies to substances containing single bonds. One must be careful not to try to apply it to substances involving double bonds or triple bonds because the double bond and the triple bond have characteristic bond energies associated with them.

We have talked about ionic bonds and about covalent bonds and about bonds that represent resonance between ionic bonds and covalent bonds, bonds with partial ionic character. This doesn't exhaust modern valence theory. There are still such questions of what is the nature of the bond that holds together the copper atoms in a copper crystal, where each atom is similarly situated with respect to its twelve neighbors? Or what about the hydrogen bond? What about oxidation numbers of atoms? Well, it is questions of this sort that we shall come back to in our next lecture.

Linus Pauling: Now, why is it that ice has lower density than water; that ice floats? We may say, why is it that ice forms in the world as it is now, with the Earth the proper, the distance as it is from the sun? This is another peculiarity of water. If we consider water, compare water, hydrogen sulfide, hydrogen selenide, hydrogen telluride, the hydrogen compounds of the elements in this, group six of the periodic table, we see that hydrogen selenide, hydrogen telluride, hydrogen selenide, hydrogen sulfide, are gases at room temperature and they, the boiling points, are decreasing in such a way that by extrapolation, we would predict for water a boiling point of about minus one hundred degrees centigrade rather than plus one hundred degrees centigrade.

It is the fact that hydrogen bonds are formed between the water molecules that causes water to have such a high boiling point and melting point relative to other substances with the same molecular weight.

The hydrogen bond in water is an interaction. An interaction of the proton of a water molecule, the hydrogen atom of a water molecule, with an unshared electron pair of another water molecule. And, each water molecule can form four such hydrogen bonds. Here, a hydrogen bond can be formed using the proton of another oxygen atom, another water molecule, here too, and here a hydrogen bond using the proton of this oxygen atom.

In order that a hydrogen bond be formed, there must be available an electron pair, an unshared electron pair of one atom, and a hydrogen attached to another atom that is sufficiently electronegative so that there is some positive charge on the hydrogen atom. The structure of the hydrogen bond can be thought of as involving in part electrostatic attraction of the proton when we have, consider, the bond to be ionic, it is about thirty percent ionic, and the electron pair, in part, the formation of a weak covalent bond between, involving this pair of electrons and the proton when this pair of electrons is not involved in bonding.

The structure of ice, as determined by x-ray diffraction, is shown by this model. Here, the oxygen atoms are arranged in a way resembling the arrangement, not identical with, but resembling the arrangement of carbon atoms in diamond. This oxygen atom is surrounded by four other oxygen atoms at tetrahedron corners. It forms four hydrogen bonds, two using its own hydrogens, two using the hydrogen atoms of adjacent water molecules.

Closest packing of water molecules would involve ligancy of twelve for each oxygen. Here we have only ligancy four and it is because of the low value of the ligancy four that this structure, the structure of ice, corresponds to a low density.

The energy of the hydrogen bond, O-H-O, in ice and water, there are still hydrogen bonds in liquid water, about three quarters as many as in ice. The energy is about five kilocalories per mol of hydrogen bonds, that is about ten per mol of water molecules. It is this extra stabilization of liquid water and crystalline water that gives rise to the high melting point and boiling point of the substance, and of course, the hydrogen bond is responsible also for many other properties, characteristic properties, such as the very high dielectric constant of water. Only the most electronegative atoms form hydrogen bonds: fluorine, oxygen, and nitrogen.

The human body is made up largely of compounds of fluorine, not fluorine, of nitrogen and oxygen, and carbon and hydrogen, and many of these molecules interact with one another through the formation of hydrogen bonds. I believe that as our understanding of the structure of molecules, of chemical valence, including such weak interactions as the hydrogen bond, becomes more and more extensive and more and more precise, as we obtain a knowledge about the molecular structure of the human body, we shall be able to make more and more progress in the fields of biology and medicine and that this aspect of chemistry, structural chemistry, will be found to be, provide the basis for a significant contribution to the welfare of man, to human happiness.

Linus Pauling: During the preceding two lectures, we have discussed the electronic structure of atoms and molecules and some aspects of valence; ionic valence involving a transfer of electrons from one atom to another, covalence, the sharing of a pair of electrons between two atoms, normal covalence if the atoms are atoms of the same element...Covalence, with some ionic character, if the atoms are atoms of different elements with different electronegativities. This, the idea, this idea, the idea of covalent bonds with partial ionic character, is one illustration of the progress in chemistry that has been made because of the development of the theory of resonance.

Now, we want to take up some other aspects of the general subject of valence and molecular structure, aspects such as ligancy or coordination number. Metallic valence, the nature of the forces that hold atoms of copper together in the metal copper. Oxidation numbers, a part, an idea in the field of valence theory that is useful in balancing oxidation-reduction equations. The hydrogen bond, well, this is getting us into the question of the weak forces that operate, the relatively weak forces that operate between molecules.

Now, let me mention two or three aspects of covalence. I have here a model of sulfur, the sulfur molecule, S_8 , as it appears in ordinary rhombic sulfur. It fits in very well with the general theory of valence that we have discussed. I can't draw the whole ring, we have each sulfur atom forming two bonds and having two electron pairs. These are the four orbitals that correspond to the argon shell. Sulfur has completed its argon structure in forming a molecule of this sort.

Hydrogen chloride is a molecule that I mentioned, HCl, in which we have a covalent bond with about twenty-percent partial ionic character. I want to mention that we must not confuse partial ionic character in the hydrogen chloride gas molecule with the ionization of hydrogen chloride, hydrochloric acid, in aqueous solution. These are two different matters. In aqueous solution, hydrogen chloride, hydrochloric acid, is a strong electrolyte, completely ionized. It forms hydrogen ions or, perhaps we should say, hydronium ions in which a hydrogen is attached, an extra hydrogen ion is attached to a water molecule, oxygen has completed its octet, just as in water itself, but in this case it has the neon structure, just as in water itself, in this case it has three unshared – three shared pairs and one unshared pair in the neon valence shell.

A related question is the question of the use of orbitals that are not involved in the valence shell of the nearest noble gas, the noble gas with somewhat larger atomic number. Let me use silicic acid and the, the related acids, phosphoric acid, sulfuric acid, perchloric acid as an example. Silicic acid is $SiOH_4$ and we can draw a structure for it in this way, as G. N. Lewis first did, in which each of the oxygen atoms has achieved the helium, the neon structure. In the same way for phosphoric acid, we can show P, O, O, OH, OH. For sulfuric acid, S, O, O, H, H, O, and perchloric acid, Cl, OH, O, O, O. In each of these structures, the central atom is shown as having achieved the argon configuration of electrons. But, the interatomic distances observed for these acids are such as to indicate that there is a considerable amount of double-bond character in the silicon-oxygen bonds, the phosphorous-oxygen bonds, the sulfur-oxygen bonds, and the chlorine-oxygen bonds. This double-bond character could be achieved by making use of orbitals that are in the next shell beyond the argon shell.

I may make mention of the acid strengths of these acids. There is a simple consideration that leads to an understanding of the observed acid strengths. Silicic acid, H_4SiO_4 , is a very weak acid, only a little stronger an acid than water itself. Now here we have an OH. If the hydrogen ion ionizes away, this ion is left with a negative charge and it is the attraction of this oxygen for the hydrogen ion that makes the acid a very weak acid. If, however, the hydrogen ion ionizes away from phosphoric acid, we see that there are two oxygens left that are equivalent to one another so that we might say that there is a charge of minus one-half, the total charge minus one of H_2PO_4 is divided between these two oxygens. Neither one of them attracts the proton, as it approaches, so strongly as this one oxygen with charge minus-one attracts the proton in silicic acid, and in fact, phosphoric acid is much stronger than silicic acid – it is still classed as a weak acid.

When sulfuric acid ionized, we can say that there is a charge of minus-one-third on each of these three oxygens of the HSO_4 ion, HSO_4^- ion, and so there is a still weaker attraction for the proton as it approaches, as it is attracted to all three, no one of them so strongly as in the H_2PO_4^- ion. Sulfuric acid is classed as a strong acid, and of course with perchloric acid, when the proton ionizes away, we have a charge of minus one-quarter on each of the oxygens. Perchloric acid is a very strong acid.

Linus Pauling: This simple consideration applies also to acids of other sorts: boric acid, H_3BO_3 , is a very weak acid because it has only OH groups attached to the central atom. A standard example of a molecule that exceeds the octet is phosphorous pentachloride, PCl_5 . The conventional formula, structural formula for this molecule, is the one shown here in which each chlorine atom has achieved the argon structure. It is known that the molecule has the configuration of a trigonal bipyramid: two chlorines above, three around the equator. The structure as indicated here causes phosphorous to form five bonds and this would require that phosphorous make use of one orbital beyond the orbitals in the argon shell, four orbitals in the argon shell.

This, however, is not the only structure that we may write for phosphorous pentachloride. We may write a structure such as this one; three chlorines bonded around the equator, the atoms of course must be in the same position for electronic resonance, resonance of the bonds, and a chloride ion in this position, a positive charge on the phosphorous atom, this P^+ , positively charged phosphorous, is now forming four covalent bonds using only the four orbitals of the argon shell and one ionic bond. There are five structures of this sort in which the five chlorine atoms are successively given a negative charge, given a negative charge, and a resonance structure involving all of these introduces just about the right amount of partial ionic character to the phosphorous-chlorine bonds, that would be sixteen percent of partial ionic character to the phosphorous-chlorine bonds, corresponding pretty well to the difference in electronegativity of phosphorous and chlorine in the electronegativity scale.

There is another aspect of valence theory that I should like to discuss now. This is ligancy, or coordination, the coordination of several atoms or groups of atoms around the central atom. For example, here in the sodium chloride crystal, we have sodium ion that, where is it, sodium ion surrounded by six chloride ions in an octahedral arrangement, chloride ions surrounded by six sodium ions. It is customary to refer to the cation usually as the coordinating ion and to say that sodium has ligancy six in the sodium chloride crystal. Its ionic valence is one. We can say that it forms six, one-sixth ionic bonds with the six surrounding chloride ions. In beryllium, in the hydrated

beryllium ion, BeH_2O four times, there are four bonds formed between beryllium and the surrounding water molecules. In the hydrated magnesium ion, MgH_2O six times, there are six water molecules around the magnesium ion located at the corners of an octahedron. In AlH_2O four times, they are at the corners of a tetrahedron. Now, the bonds between the beryllium ion, or the water, or the magnesium ion, or aluminum ion in AlH_2O six times, and the oxygen molecule, involves the electrons pairs, an unshared electron pair of the water molecule. These bonds are not, however, normal covalent bonds. They are covalent bonds with partial ionic character.

Here we have beryllium, here magnesium and aluminum in the electronegativity scale, and oxygen over at 3.5, nitrogen at 3.0. With a metal ion and oxygen or nitrogen in the water molecule or the ammonia molecule, the bonds have only one-third to one-half covalent character, two-thirds to one-half ionic character so that there is not a great amount of electric charge transferred from the oxygen atom of water or the nitrogen atom of ammonia to the central atom. In fact, the amount of partial covalent character of these bonds is just about enough to neutralize the charge on the central atom, to leave it electrically neutral. We may say that there is a sort of electro-neutrality principle operating here, that atoms strive to have zero charge rather than the charge of plus two for beryllium and magnesium, plus three for aluminum.

Linus Pauling: I should like to discuss one of the standard coordination complexes in this respect. Here, we have a model representing the complex CoNH_3 six times, triple plus, cobalt three hexammine. Six ammonia molecules attached to a central cobaltic ion. This group of atoms, this complex ion, has a total charge plus three, but this charge is not to be considered as located on the cobalt atom. If I draw the regular structure for the complex, represented as involving a cobalt ion, I can say cobalt three-plus, NH_3 out here, NH_3 . I might draw this showing covalent bonds. Then N, H, H, H, N, H, H, H, and then out in front here, N, H, H, H, and behind, N, H, H, H. Now with the charge plus three, if these were normal covalent bonds, a pair of electrons on the nitrogen would be shared with the cobalt, six electrons would be transferred to cobalt, and the charge would become minus three. But, in fact, the position of cobalt in the electronegativity scale is such that we expect the cobalt-nitrogen bonds to have about fifty percent covalent character, fifty percent ionic character.

That is just enough then. Six half-electrons transferred, half of our covalent bonds, on, in each of the six directions, to neutralize the three plus charges, leave the cobalt atom with the zero charge, and each nitrogen atom has then a charge of plus one-half. But this isn't the end of the story. The nitrogen-hydrogen bonds, as indicated by the difference in electronegativity of nitrogen and hydrogen, hydrogen at 2.1, the nitrogen-hydrogen bonds have about one-sixth partial ionic character, so that there is a charge of plus one-sixth of an electronic charge, of magnitude of electronic charge on each hydrogen atom, and this neutralizes the charge on the nitrogen, leaving it zero. Consequently, the total charge of plus three for this complex ion is divided up into eighteen little charges of plus one-sixth each which are located on the eighteen hydrogen atoms that are on the periphery of this complex. This is, of course, a nice situation because a distribution of charge of this sort corresponds to electrostatic stability.

If we have a metallic sphere that is electrically charged, all of the charge is on the surface of the sphere, even though it is a solid metallic sphere, the charge, the elements of charge repel one another until they reach the surface. In fact, I think that we may say

that in aqueous solution, the hydrogen bonds that are formed by these hydrogen atoms with surrounding water molecules neutralize these charges to some extent and put the charges in still smaller increments still farther away from the central part of this complex.

There's another aspect of the structure of this complex that I want also to mention. That is the utilization of the orbitals. Let me, let us consider the, let us consider the orbitals that are available for cobalt. In the periodic table of the elements, cobalt is seen with atomic number twenty-seven. Cobalt plus three, with three charges, well, I've erased the plus three, cobalt plus three with three electrons removed from it would have twenty-four electrons, that is, six more than the number for the argon structure. If we consider the five 3d orbitals, we may place these six electrons in three of the orbitals. Then, we have 4s and the three 4p orbitals. Here we have left on the cobalt atom, six orbitals in the argon shell, krypton shell, krypton shell is the shell with nine orbitals. Three are used by the six unshared electrons of cobalt. Six orbitals are left. These orbitals are of such a nature that they are nicely-suited to the formation of bonds, six bonds pointing toward the corners of a regular octahedron. These six orbitals are orbitals of this sort. So that we have a nice story, covering, accounting in a satisfactory way for the existence and stability of the cobaltic hexammine complex ion.

In fact, the electro-neutrality principle, the, which is the striving of every atom to achieve an electric charge that is close to zero, sometimes partial ionic character of bonds keeps it from being exactly zero, but by increasing the ligancy, one, it is often possible for the charge to be decreased closer to zero. This electro-static, this electro-neutrality principle explains in a pretty satisfactory way why it is that so many elements in the periodic table, especially in the transition region, form ions in aqueous solution with charge plus two or plus three. Iron, cobalt, nickel, copper, zinc, manganese, chromium, the principle ions, cations, of these metals are those in which the charge on the ion is plus-two or plus-three. These metals all have electro-negativity around in this region. The amount of partial covalent character of the bonds is somewhere around one-third to one-half, which is just enough, with octahedral coordination, to neutralize the charge of plus two or plus three on the central ion and move the charge out toward the periphery of the hydrated ion in the case of an ion in aqueous solution.

Linus Pauling: There is another aspect of the theory of valence that I should mention now, and this is one that has been understood, at any rate understood to the extent that we shall discuss now, only during the last few years. This is the matter of metallic valence.

What is it? What is the nature of the forces that hold the copper atoms together in the metal copper, in the crystal of copper? Well, let us consider copper. I think that I would prefer to consider aluminum. Let us consider the metal aluminum. It has the same structure as copper – cubic closest packing as shown here. Each atom of aluminum has, each atom of aluminum here is surrounded by twelve neighbors that are equally distant from it; six in this layer, three in the layer behind, three in the layer in front.

Now, aluminum has atomic number thirteen. It has three electrons outside of the neon shell, plenty of orbitals, four orbitals in the argon shell, so that we would expect it to form three covalent bonds using its three electrons. In order that it be bonded equally to

twelve neighbors, we may describe the three bonds as resonating among the twelve structures and holding the aluminum atoms together.

The same sort of resonance of covalent bonds among a large number of alternative positions occurs in other elements. For example, in the metals potassium, calcium, scandium, titanium, vanadium, chromium, the properties of these metals correspond nicely to the idea that we have one, two, three, four, five, six electrons, six bonds formed by each atom and resonating around the positions connecting the atom with the neighboring atoms. The malleability and ductility can be understood in terms of this resonance, also the property of electric conduction, the ability of the metal to conduct the electric current. I may mention that there are two kinds, or two common kinds, of closest packing of spheres that are represented by the metals. In, this is cubic closest packing, analogous to this structure, along a three-fold axis of the structure, there is repetition after three layers. There are two alternative ways of placing any layer above the layer beneath it: this way, or this way. In cubic closest packing, these layers, these ways, repeat so as to give repetition after three layers, in hexagonal closest packing, there is repetition after two layers. This gives a hexagonal crystal. Magnesium and many other metals have this structure. Aluminum, copper, silver, gold, many other metals have this structure, cubic closest packing.

I think that it is interesting that in 1890, many years before x-ray diffraction was discovered, the English amateur scientist, William Barlow, had assigned this hexagonal, closest packed structure to magnesium on the basis of the knowledge that magnesium crystallizes at hexagonal crystals, with the right, with a certain dis-, ratio, this distance to this in the crystal, and had assigned cubic closest packing to aluminum, copper, silver, gold, and other metals. In fact, he had assigned the sodium chloride structure to sodium chloride and other alkali halogenides, the cesium chloride structure to cesium chloride, the sphalerite structure to the cubic form of zinc sulfide, the wurtzite structure to the hexagonal form of zinc sulfide, the fluorite structure to fluorite, CaF_2 , and he was right on all of these assignments. He wasn't, wasn't sure, of course, that he was right, but it has turned out that his ideas about closest packing of spheres and so on were right and permitted him to find the correct structures.

Linus Pauling: A very important use of valence, old fashioned valence, was in balancing equations for oxidation-reduction reactions. Now that valence, the old idea of valence, has been replaced by a number of new and more precise concepts, we have still a problem of doing something about oxidation-reduction reactions, and this problem has been solved by introducing another concept, the concept of oxidation number.

Oxidation numbers assigned to atoms permit us to keep track of the electrons in an easy way. Whereas the other aspects of valence that we have been discussing are less, are less artificial, are really an effort to understand what nature is like, just what the electrons are doing in a complex such as the cobaltic hexammine ion, oxidation number is, by nature, artificial. It is something that we introduce with the use of certain rules.

One of the rules about oxidation number is that in a, in an element, the oxidation numbers of the atoms are zero. For example, in the chlorine molecule, Cl_2 , each chlorine atom started out with seventeen electrons, two of the electrons are shared, but we split those two electrons between the two atoms so that each atom still has seventeen, no resultant charge, and we say that for Cl_2 in Cl, the oxidation number of each atom is

zero. Similarly for hydrogen, similarly for copper, or aluminum, or any other metal, the electrons are divided up equally among the atoms, and in as much as each atom is, in as much as the whole metal is electrically neutral, the individual atoms must be electrically neutral too.

In the case of a molecule such as H_2O , O, H, H, the electrons that are shared between two atoms of different elements, oxygen and hydrogen, are assigned to the more electronegative of the elements. Now, oxygen, you remember the electronegativity scale, oxygen is more electronegative than hydrogen. We assign these electrons to oxygen so that oxygen becomes O-2, hydrogen is H plus one. The sum of the oxidation numbers in the molecule must add up to zero because the molecule is electrically neutral. If we consider the hydronium ion, H, H, H, here, the hydronium ion that has a plus charge, again we assign the electron pairs that are shared with hydrogen to the oxygen atom. Oxygen has oxidation number minus two, hydrogen plus one, hydrogen plus one, hydrogen plus one, and, the sum of the oxidation numbers for all the atoms adds up to plus one, which is the charge on the complex ion.

With, now, hydrogen peroxide, H_2O_2 , the oxidation numbers can be assigned in either one of two ways. We may say that hydrogen has oxidation number plus one, the two oxygen atoms are equivalent, therefore in order that the molecule be electrically neutral, oxygen must have oxidation number minus one. Or, knowing the structure of the molecule, it has this structure, in fact, it is known that there is a dihedral angle between the H-O-O plane and the other H-O-O plane about us shown here. O-O, distance, well, I don't, 1.47 angstrom, O-H distance, .96 angstrom, and so on, and the electronic structure that we can assign to it is this one. This pair of electrons is to be assigned to this oxygen atom. The shared pair split so that this oxygen atom has a total of seven, one, two, three, four, five, six, seven, yes, seven electrons surrounding the nucleus, and of course, the two electrons of the helium shell also. This means that the oxygen atom ends up with a charge of minus one. The oxidation number of oxygen is minus two in almost all oxides. Minus one in the peroxides were there is a O-O single bond, and zero in the elementary substance.

We can discuss oxidation numbers of other elements without discussing, in certain compounds, without discussing the distribution of the electrons. For example, consider the permanganate ion, MnO_4 with a charge of minus one. Oxygen, this is not a peroxide, the properties are not those of a substance containing an oxygen-oxygen single bond, and so we assign to oxygen the oxidation number minus two. There are four of these oxygen atoms. This gives a total eight negative charges; one of them still remains in the ion itself. Hence, manganese must be plus seven.

Well, of course, with the electronic structure, whatever the electronic structure is, each oxygen atom must have four electron pairs in its valence shell, either shared or unshared, some of them probably shared with manganese, but oxygen is much more electronegative than manganese, manganese is somewhere in this region, so that we would assign these electron pairs to oxygen and not to manganese. All seven valence electrons of manganese have been taken away from it, it is manganese with oxidation number plus seven.

Linus Pauling: Now, the assignment of oxidation numbers to the atoms in a molecule or complex ion, having been made, we may go ahead with the job of balancing the equation for a reaction.

Let us take, well I've been talking about hydrogen peroxide, I remember a nice oxidation-reduction reaction that involves hydrogen peroxide. If one has hydrogen peroxide in a beaker with some sulfuric acid, and then adds potassium permanganate, that is, adds the permanganate ion, a beautiful magenta color, the permanganate ion is destroyed, as shown by the loss of color, and oxygen is evolved. Hydrogen peroxide is oxidized by the permanganate ion in acid solution.

Of course, to write the equation for this reaction, we need to know what it is that is reacting and what the products of the reaction are. The way to find out is by experiment. Or, if somebody else has carried out the experiment already, by reading a textbook, or a paper in a journal, and if the statements made in the textbook and paper are reasonable, they can be accepted. Now, in this case, permanganate ion is reduced by the hydrogen peroxide to manganous ion, Mn^{++} , and hydrogen peroxide is oxidized to oxygen. You can see bubbles of gas coming out of the reaction mixture and you can identify this gas easily as oxygen.

I like to balance oxidation-reduction reactions, I like to balance the equations for oxidation-reduction reactions, by writing electrode reactions. For example, let us take H_2O_2 and say that it forms hydrogen ions plus oxygen...which escapes. Now, let us assume that this reaction is taking place by itself, perhaps in an electrolytic cell where there are electrodes present that can provide electrons or take up electrons. Here, I have started to write the electrode reaction, but there is not conservation of electric charge. Hydrogen ions are formed so that I can write plus two electrons to conserve charge, and now everything is conserved. Hydrogen atoms are conserved because I wrote two in front of the H^+ , oxygen atoms are conserved, and the electric charge is conserved, which means electrons are conserved. The oxidation number of hydrogen is plus one, that of oxygen minus two. Hydrogen, again, is plus one here, so that there has been no change in valence in oxidation number of hydrogen. But, here, oxygen is minus one. This is a peroxide.

Oxygen has changed from minus one to zero, and if I look at the atoms that have changed their oxidation number, I see that two oxygen atoms have gone up from minus one to zero, which means that two electrons have been given off, and they are indicated here, so everything is rosy.

Now, the other reaction, with the permanganate ion, we can write as an electrode reaction too. This one is so simple that you don't need to have any rules. This one is a little more complicated. Here, permanganate is reduced in acid solution to the manganous ion, bipoisitive manganese. In the permanganate ion, oxygen has oxidation number minus two, manganese plus seven, so that manganese has changed by five. This means that we need five electrons in order to carry out the reduction of manganese, the deelectronation, the electronation of manganese from plus seven to plus two. Two charges over on this side, plus seven, minus five gives us...oh, this is minus one, minus five and minus one is six over here. We need a total of eight plus charges. This is in acid solution so I write plus eight plus, with hydrogen ions. And now, to balance the atoms, I have plus four H_2O .

These two electrode reactions can be combined with one another if we make the same number of electrons used up in this reaction as formed in this reaction. I think that I can multiply this reaction by five and this one by two without making any mistakes and write two MnO_4^- plus five H_2O_2 and here there would be five, ten electrons that balance the two electrons. Sixteen H^+ and ten H^+ leaves plus six H^+ to form two Mn_{++} plus five O_2 that comes off plus eight H_2O .

This should complete the reaction. There should be conservation of charge, two minuses and six pluses and four pluses, and there are the four pluses, conservation of manganese atoms, conservation of oxygen atoms. Here are all together eight and ten is eighteen, there are eight and ten is eighteen. And conservation of hydrogen, ten and six, sixteen and a total of sixteen over there, so that we have succeeded in balancing this equation.

Linus Pauling: The...next topic that I want to talk about deals with rather weak forces, the forces that operate between molecules, holding them together, but that are not considered to involve valence bonds of the ordinary sort. Water is a very good example of a substance for discussion because the properties of water are determined by a weak, or rather weak force of a special sort, the force that is involved in the hydrogen bond. The hydrogen bond was, I think it is proper to say that it was discovered by Latimer and Rodebush, two professors in the University of California in 1922, and it is a very important part of structural chemistry.

Let us consider water and ice, the ordinary form of crystalline solidified water. I should have brought along a bucket of water and a cake of ice to illustrate this part of the talk, but you know what water and ice are like. In particular, you know one of the peculiar properties, almost unique properties that water and ice have. Ice, the crystalline form, is less dense than water the liquid form. So that, water, it is eight percent less dense, so that a cake of ice floating in water, an iceberg floating in water, have eight percent of its volume projecting above. Well, of course, icebergs usually float in salt water, that means, density of salt water is greater, about twelve percent of the iceberg projects above the surface of the ocean. This is a very valuable property that water has. It means that when ice forms on a lake or on the ocean, it forms on top rather than on the bottom, so that in the summertime the ice can melt. We do not have the situation that our oceans and our ponds are solid ice from the bottom up and only a little bit of the surface melts into liquid water in the summer.

This was, this fact was mentioned by John Tyndall, an English scientist in the Royal Institution about seventy-five years ago, when he said this unique property of water, of expanding on freezing, illustrates the beneficence of the creator. He, of course, was not quite right in calling it a unique property because a few other substances have been found that have the property of expanding on freezing. One of them is antimony.

Well, in a sense, the fact that antimony expands on freezing also illustrates the beneficence of the creator. After they developed the invention of printing, type is made not from lead, but from a lead-antimony alloy. Lead contracts on freezing and if molten lead were poured into the matrix, the mold, to make the typeface, as it shrunk away from the typeface, it would shrink in different ways so that one had a poor impression of the matrix and the printed page would not be very clear. By adding antimony to the lead to make an alloy that does not shrink, the antimony counteracts the effect of the lead,

the alloy does not shrink As it solidifies it gives a good sharp impression, through the type from the matrix, and the printed page is correspondingly beautiful and clean.

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