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# Nobel Prize in Chemistry 1949

**William Francis Giauque**

The Nobel Prize in Chemistry 1949 was awarded to William F. Giauque *"for his contributions in the field of chemical thermodynamics, particularly concerning the behaviour of substances at extremely low temperatures"*.

## RESEARCH INFORMATION:

Chemistry has its origins far back in the cultural development of mankind. The search for the laws governing the structure of and changes in the material universe has followed many, now and then rather curious, paths. The alchemist's dream of making gold or of finding the philosopher's stone led to experiments which would be today regarded as unmethodical, but which nevertheless led gradually to a pretty thorough knowledge of the diverse properties of matter. The driving force behind this research was not only personal gain or a desire to please the aristocratic patrons who often had to pay for the experiments, but a genuine thirst for knowledge.

Chemistry became a science only when experiments became systematic and an attempt was made to discover general laws for the changes in matter. A scientific law should not only render possible a coherent account of all known natural phenomena, but should preferably enable us to predict new ones. When chemists today grope their way forwards in unknown fields, they must always, like the alchemists, try by means of experiments to determine what can and what cannot be done. But they are enormously helped by certain exact general laws which make it possible to predict the result of a chemical reaction under varying external conditions, for example different pressures and temperatures. To be able in this way to foresee the result of a chemical reaction is naturally of immense practical value. It is thus often possible nowadays to calculate in advance whether a given chemical process is possible and what conditions favour it. But such laws are also, of course, the basis of any comprehensive picture of the chemical processes in our world, so that research into them has occupied a central position ever since chemistry became a science.

The laws which I want particularly to touch on here are those dealing with the kinship between substances or, as chemists say, their affinity to one another, how this affinity shall be defined, how best to measure it and to what extent it can be calculated. When a lump of coal burns in air, heat is generated. The chemical reaction which takes place is that the coal combines with the oxygen in the air to form carbon dioxide. It was natural that the quantity of heat thus generated was first of all thought to be a measure of the affinity - one would of course expect that the greater the tendency for the reaction to take place, the greater would be the heat. This is often but not always the case. Chemical reactions are known which cause a reduction in temperature. The heat generated during a reaction is not, therefore, suitable as an exact measure of the affinity. It has been discovered that we should measure instead the so-called free energy of the chemical reaction, i. e. the part of the total energy liberated during the reaction that can be used directly or indirectly for the production of mechanical or electrical energy. This free energy can be measured exactly by mechanical, electric or spectroscopic methods, but only under conditions which are normally not very easy to establish - it is necessary, for example, for the reaction to be studied in equilibrium. It is usually far simpler to measure the heat generated during a chemical reaction, the heat of reaction, and it is therefore natural that much research in this field has been devoted in the last fifty years to the problem of finding some way in which the free energy may be calculated from the heat, i.e. to enable us to predict the result of a chemical reaction from purely thermodynamic determinations.

One of the most brilliant scientists engaged in this research, and perhaps the foremost pioneer in chemical thermodynamics, was an American, Willard Gibbs, who worked at the end of the last century. He formulated clearly the equation which tells us that what we need to know, in order to calculate the free energy from the heat of reaction, is the change in *entropy* during the reaction. This change in entropy, multiplied by the absolute temperature, must be added to the heat of reaction in order to give the free energy.

This year's Nobel Prize winner, William Francis Giauque, has added considerably to our knowledge of the entropy of chemical substances, particularly at very low temperatures. I shall try to give you an idea of what entropy is, but first I must explain that one cannot observe it as one can, for example, temperature and pressure, and that even students of chemistry fight shy of this concept to begin with. If a substance is given a certain quantity of heat, then the entropy increases by an amount equal to the amount of heat divided by the absolute temperature. We can thus measure the change in entropy, and from these measurements obtain the data necessary for us to calculate the free energy and heat of reaction of a chemical reaction at a given temperature if we know them at another temperature. Entropy is an extraordinarily interesting property of a substance, particularly in the light of the molecular and atomic theories. We thus know that what we call heat is the result of the motion of the molecules. A higher temperature corresponds to a more lively molecular motion. Entropy, again, is a measure of the state of molecular disorder. If we melt an ice crystal by heating it, the entropy increases by a quantity equal to the melting heat divided by the absolute temperature, and the almost perfect order of the water molecules in the ice crystals changes into the disorder prevailing in the water formed by the melted ice.

There is a general law that all spontaneous chemical and physical processes are associated with an increase in entropy. We must conclude, therefore, that the world is becoming more and more disordered - a conclusion which is naturally only proved for molecular processes.

There is another very important law stating that the entropy is zero for a crystallized substance at a temperature equal to the absolute zero,-273.16°.

This law - the third law of thermodynamics - first formulated by the German Nobel Prize winner, Walther Nernst, has only now been fully proved as a result of Giauque's work. By means of this law we can now calculate not only differences in entropy but the entropy itself for a considerable number of elements and chemical compounds. Thus, if we want to calculate the free energy necessary for the formation of, for example, a certain organic substance made up of carbon, hydrogen, oxygen, and nitrogen, we look up the entropies of these elements in a table and determine in addition the heat of formation and the entropy of the compound. The problem of calculating the chemical affinity from the heat of formation or the heat of reaction is therefore solved in principle.

Behind the data used in such calculations and behind the final proof of the third law lie, however, extensive studies of the properties of substances at temperatures approaching absolute zero. It is here that this year's Nobel Prize winner has made his greatest contributions to chemistry. By supreme experimental skill he has overcome the many great difficulties which must obviously be inherent in investigations under such extreme conditions. He has also worked out new methods for experiment in this field, of which his magnetic cooling method deserves special mention. This method has made it possible to reach temperatures nearer to absolute zero than was possible by any earlier technique.

Giauque's method is based on the fact that the crystals of certain substances (e.g. gadolinium sulphate) when magnetized at low temperatures, can be brought to a higher degree of molecular order. Heat is liberated and led off in a bath of liquid helium at a temperature of 1° above absolute zero. After the liquid helium has been pumped away, so that the crystals are heat-isolated, the magnetic field is removed and the temperature falls to only some thousandths of a degree above absolute zero. The method is already widely used in a number of low-temperature laboratories in various parts of the world, and important discoveries in superconductivity and the magnetic properties of substances have been made with it. Giauque first mentioned the idea at a Congress of the American Chemical Society on the 9th of April, 1926. But not until 1933 did he have the necessary experimental resources to be able to realize his project. Characteristically enough, Giauque states himself that the first successful attempt was carried out between 3 a.m.and 9 a.m. on the morning of the 19th of March, 1933.

It should be mentioned that Giauque has also worked out important methods for measuring temperatures accurately just above absolute zero. In order to appreciate fully the importance of the fact that this temperature range has been opened up for research, one must understand that the properties of substances change just as much between 1° absolute and 0.003° absolute as they do from room temperature down to 1° absolute. Moreover, many natural phenomena become simpler when the motion due to heat has almost ceased and the molecules have lain down to rest. Giauque's contribution to chemistry has, thus, opened up a fascinating field for research where he, with his co-workers, has achieved most important results. In this entropy measurements he has succeeded in reaching an accuracy ten times greater than that of the best earlier measurements, thus creating the pre-requisite conditions for the fundamental results already mentioned: the proof of the validity of the third law and the accurate calculation of chemical equilibria. A number of different substances were used in these studies. I shall mention here only the beautiful investigation of the equilibrium between nitrogen oxides and between different hydrates of nitric acid. The investigations on the entropies of the pure metals are also of great interest. Determining the difference in entropy between the glass form and the crystalline form of glycerine - a problem which Giauque dealt with as long ago as in his doctor's thesis in 1923 - is particularly important in testing the third law.

Giauque has achieved many interesting results by comparing the entropy values he has obtained by these methods (calorimetric entropy) with the values he could calculate from the band spectra (spectroscopic entropy). The latter method was introduced by the Nobel Prize winner James Franck and by the American physicist Birge. But Giauque has worked out practical methods for calculating the thermodynamic constants from the spectra. Here, as so often elsewhere in research work, a comparison between accurate data obtained by fundamentally different methods has given rise to interesting new discoveries. Giauque was able to explain the difference between the entropies thus found for carbon monoxide. The difference between the two ends of a carbon monoxide molecule is so slight that it can lie orientated in two directions in the crystal. Giauque has demonstrated this interesting effect in a number of substances with a greater or lesser high degree of symmetry in a series of papers published at the beginning of the thirties. These results, like so many others of Giauque's, are clear examples of the relationship between entropy and the degree of molecular disorder, a fact which I have just tried to explain.

In connection with such spectroscopic experiments, Giauque and Johnston made in 1929 the remarkable discovery that the element oxygen does not only consist of atoms with atomic weight 16 but contains in addition small quantities of oxygen isotopes with atomic weights 17 and 18. Since the atomic weight of oxygen is the basis for the calculations of the atomic weights of all the other elements, this discovery is of fundamental interest and also gave rise to similar investigations with other elements.

Giauque's achievements in the field of chemical thermodynamics and especially his work on the behaviour of matter at low temperatures and his closely allied studies of entropy comprise one of the most significant contributions to modern physical chemistry. The Royal Swedish Academy of Sciences derives great satisfaction from being able to reward this work with the Nobel Prize for Chemistry.

***<u>For more details please visit:</u>***

http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1949/press.html