The Problem of the Chemical Origin of Solar Radiation*

In View of Facts That Make Physical Explanations Unsatisfactory

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AMONG the numerous problems of astro-physics whose solution is a thing of the future, that of the origin of the solar radiation has been one of the most freely controverted. More and more, of late years, astronomers are abandoning the attempt to account for this phenomenon on purely mechanical or physical grounds, and are falling back upon the reactions of chemistry to explain the mystery.

An investigation of this sort should naturally be undertaken with a certain degree of diffidence, since we are forced by the very nature of the case to extend into a domain inaccessible to direct experiment laws verified for intervals of temperature and pressure relatively limited. In spite of this it seems that the modern theories of physical chemistry may be consulted to good result in this connection, with the well understood reservation that new discoveries are liable to modify more or less any conclusions that may be formed. It is with this point of view that we propose to discuss the problem.

First let us state clearly its terms. The radiation of the sun is of such magnitude that each gramme of its enormous mass loses annually almost two calories of heat. At this rate, even though the solar matter possessed a very high specific heat and an enormous mean temperature, the complete refrigeration of the sun should be a matter of only a few thousand years at most. But since the radiation in question has continued without appreciable change throughout the stretch of historical time, and indeed throughout a great part of the stretch of geologic time, we are forced to believe, as Arrhenius so tersely puts it, that "our sun, in his debit and credit account, must have some source of income approximately equal to his apparent expenditures."

R. Mayer has supposed that the radiation is maintained by a continuous shower of meteorites upon the surface of the sun; but his hypothesis has slight intrinsic probability, and in addition meets insurmountable astronomical objections. Helmholtz, and later Lord Kelvin, have sought for the origin of this great store of energy in the contraction of the sun. But the calculations of these scientists do not permit us to fix at more than fifty millions of years the interval during which solar illumination of the earth would be possible; and, speaking geologically, this is not enough. Other physical explanations are equally unsatisfactory; so we are forced to inquire whether the key to the mystery does not lie in the reactions of chemistry.

To understand well the exigencies of the problem presented the chemist by this question, it may be recalled that a block of carbon of mass equal to that of the sun would be consumed in less than five thousand years if, by conversion into carbonic acid, it were to feed the solar radiation. In the presence of this fact, it obviously becomes difficult to find, in the current phenomena of chemistry, a satisfactory explanation. Nevertheless, the astronomer Faye attempted, in 1877, to construct a theory on this basis. He supposed that in the interior of the sun, by reason of a very high temperature, all substances exist only in an elementary state; and that, coming to the surface, these elements enter into a multitude of compounds, with tremendous and continuous liberation of heat. But aside from its inability to measure up to the test of numerical computation, this hypothesis is met by two capital objections. In the first place, the action which it postulates would certainly be accompanied by a return of the compounds formed to the center, there to be dissociated with absorption of energy equal in amount to that previously liberated. And in the second place, the existence of compounds at the sun's surface is in disagreement with observations made to the effect that the solar atmosphere consists entirely of uncombined elements. Then, too, it could be urged that the great viscosity of the central regions would present great resistance to this continual circulation of matter.

Recently, however, following the discovery of radio-active matter and the study of its properties, it has seemed that the liberation of solar energy could be accounted for, at least partially, by the assumption of a large reserve of radio-active substances stored up in the solar mass. With what we know of radium, it would suffice for the feeding of the radiation that each kilogramme of this mass contain two milligrammes of that element. This explanation, however, turns out to be no more acceptable than the others. According to Arrhenius, it implies either that heat is created out of nothing, or that the radium receives from space some radiation

which it absorbs and then transforms into heat. Besides, the life of radium is limited; according to recent estimates, it loses half its radio-activity in seventeen hundred years. So this suggestion is outlawed.

Impelled by the insufficiency of these various explanations, Arrhenius has set himself to the search for another source of the sun's energy, and has developed a theory of which we indicate the principal features. In the outer portions of the sun matter is found in an elementary state only, while deeper down it exists in the form of compounds; this much is established spectroscopically. Now as we penetrate into the interior of a star, the temperatures and pressures increase until they attain the inconceivable magnitudes of 6,000,000 degrees and 10,000,000 atmospheres, respectively. Under these conditions matter, even though gaseous in form, is strongly viscous.

Arrhenius assumed that at such extreme temperatures and pressures all matter must become gaseous. Now it is true that there exists a so-called critical temperature characterizing every liquid, in passing which that liquid will always take the gaseous form, however high the pressure to which it be subjected. And since the critical temperatures of the less volatile substances do not probably exceed 10,000 degrees—that attributed to platinum is about 7,000 degrees—we might conclude, at first glance, that above such a temperature all matter is necessarily gaseous. But it turns out that such necessity does not exist. It is now found that matter may revert to the solid form at temperatures above its critical point, under pressures sufficiently great.

This phenomenon has been produced experimentally with chloride of phosphonium and with carbonic acid. The former, as Guillaume has been able to show, becomes solid again at 102.4 degrees, although its critical point is only 49.1 degrees. But in the gaseous state (Briner), and probably also in the liquid, this compound is dissociated; so there is some question as to whether its critical temperature is properly comparable with that of a more stable substance. This doubt does not appear in the case of carbonic acid. Under pressures greater than 6,000 atmospheres, according to recent experiments of Bridgman, this acid, whose critical point is 31 degrees, presents unmistakable evidences of solidification at all temperatures. It must, therefore, be admitted that matter could exist in a solid state in the interior of the sun, in spite of the high temperature there ruling. The only question—and one, of course, difficult or impossible to answer—is whether the strong pressures there exercised are sufficient to overcome the high temperatures to the extent of making this solid condition possible.

It is clear that if the sun were thus a solid globe at the point of incandescence, we would have at once an explanation of the continuous spectrum which it gives. But the continuity of the spectrum does not of itself imply a solid (or liquid) state. Gases, at sufficiently high temperatures, in sufficient thickness, and under sufficient pressure—conditions all realized in the sun—might very well afford a continuous spectrum. So we have no conclusive evidence for or against the possibility of a solid core in the sun.

With the realization, then, that the establishment as fact of that possibility would relegate it to the scrap heap, we return to Arrhenius's hypothesis. He states that at such temperatures and pressures as prevail in the interior of the sun, there should be found, according to the principles of thermodynamics, substances whose formation is accompanied by absorption of heat and contraction. Such a substance, whose formation takes up heat and whose breaking up liberates heat, is called endothermic. Reminding the lay reader that "heat of formation" signifies heat given off in formation, it is clear that the heat of formation of an endothermic substance is negative. Following Arrhenius, we give as examples of such substances ozone, with heat of formation —36,200 calories; nitrogen proto-oxide, —18,000 calories; nitric oxide, —21,000 calories; nitrous anhydride, —6,800 calories; nitrogen peroxide, —7,700 calories; carbon disulphide, —28,700 calories; cyanogen, —71,000 calories; nitrogen sulphide, —31,900 calories; selenium sulphide, —46,200 calories. He mentions also the compounds of chlorine with nitrogen, and of hydrogen with sulphur; and he asserts that in addition to such substances of relatively simple constitution, others would be formed which, by reason of the extremely high temperature, would possess a degree of endothermicity beyond all comparison with known substances. He concludes: "It should then be clear that

in the central part of the sun there exist substances which, when brought to the surface, decompose with great liberation of heat and great increase in volume. We must consider these as explosives of enormous power, beside which dynamite and picric acid are mere playthings. Phenomena of this sort would be capable of supporting the sun's radiation for billions and trillions of years."

The theory proposed by Arrhenius is without doubt very attractive, and can readily be understood to have attained a certain degree of acceptance, even in competent scientific circles. None the less, it seems hardly reconcilable with certain of the latest researches. We shall discuss the matter from the viewpoint of these, and from this discussion draw indications of the road to pursue in search of a chemical solution of the problem proposed.

We have indicated one serious deficiency in that the hypothesis is not able to substantiate the gaseous state of the sun which it postulates. Another capital objection presents itself at the very start, apropos of the endothermic compounds cited as examples. The indicated values of their heats of formation are for ordinary conditions, and not for the conditions realized in the sun. That we do not here make a distinction without a difference will be clear from the following considerations. Given an elementary gaseous medium under any pressure whatever, if the temperature be sufficiently high the molecules will be dissociated into atoms. Modern researches have shown that this dissociation is already appreciable at temperatures, high, to be sure, but still within the reach of experiment. So that in dealing with chemical action in such a mass we have more and more, as temperature increases, to reckon with the formation of compounds from atomic aggregates instead of molecular ones. This means that the heat given out in the formation of a molecule, and hence absorbed in its breaking up into atoms preliminary to recombining, need not be furnished for this particular reaction, and that therefore the heat of formation of the substance being compounded is increased by just that much. So that heats of formation of all compounds from atomic bases are much greater than the corresponding heats from molecular bases. In the case of endothermic compounds it may very well be that the heat is sufficiently greater to become positive; i. e., that when formed of matter in the atomic state these compounds are actually exothermic.

The adjoined table illustrates the point. It shows, for several elements, the coefficient of dissociation for certain temperatures—that is to say, the percentage of a given mass of the substance in question which breaks down into atoms at the given temperature—and the calories of heat absorbed by the dissociation of a gramme-molecule—in other words, the heat of formation of a gramme-molecule from an atomic base.

	Temperature.	Coefficient of Dissociation.	Molecular Heat of Formation.
			Calories.
Iodine.....	1390	66	36,800
Bromine.....	1050	6	57,000
Chlorine.....	1670	1	113,000
Sulphur.....	2177	50	120,000
Hydrogen.....	2727	6	90,000

The heat of formation of a gramme-molecule of oxygen has been found equal to 160,000 calories; that of a gramme-molecule of nitrogen is unknown, but surely exceeds 150,000 calories. With respect to nitrogen, the stability of its molecule furnishes an immediate explanation of its inertia. This is not to be confused with the case of the rare gases of the atmosphere, as argon and helium, whose atoms are destitute of chemical affinity. Such is by no means the case with the nitrogen atom, which enters into many compounds, whereas all efforts to make helium and argon react have failed.

What are the consequences of the above figures as regards chemical equilibrium? First, that when formed from atoms, all compounds without exception are exothermic. This may be shown, for example, by calculating the heat of formation, from atoms, of the endothermic substance nitric oxide. We base this calculation on the ordinary thermodynamic equation

which indicates that the reaction is accompanied by absorption of heat. Considering the molecules of this equation to have been formed from atoms, and taking account of their heat of formation, as stated above, we have

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A military aeroplane ready to start for Kut with a cargo of provisions.

A NEW USE FOR AEROPLANES.—[See page 100.]

merely to combine algebraically the above equation with the equation

$$N_2 + O_2 = 2N + 2O - 310,000 \text{ cal.}$$

getting as a result

$$2N + 2O = 2NO + 268,000 \text{ cal.}$$

whence it appears that the heat of formation of a gramme-molecule of nitric oxide from atoms of oxygen and nitrogen is some 135,000 calories—or more, since any error in the molecular heats of formation used is one of under-estimation. A similar calculation carried out for ozone shows that when formed direct from atoms this substance has heat of formation 200,000 calories, instead of the negative figure mentioned above for ordinary molecular origin.

A second consequence, following directly out of the first, is that under sufficient and continuous elevation of temperature, the formation of those compounds ordinarily endothermic, instead of being constantly accelerated, as has been supposed, eventually becomes retarded just like that of all other compounds. That is to say, so long as the substance remains endothermic, so that its formation necessitates absorption of heat, heating of the medium accelerates formation; but the moment dissociation into atoms under the influence of the high temperature has proceeded so far as to make the substance exothermic, requiring radiation of heat for its formation, further inculcation of heat of course retards that formation. The temperatures capable of producing this state of affairs, at ordinary atmospheric pressures, are not nearly so high as one might suppose; reference to the preceding table will indicate that they are without doubt inferior to those, of some 6,000 degrees to 8,000 degrees, prevailing at the periphery of the sun. In the case of hydrogen, for instance, we may place at 99 per cent the proportion of molecules dissociated into atoms at temperatures comparable to 6,000 degrees.

Consequently, contrary to the opinion upon which Arrhenius in part founded his theory, with increase in temperature alone, combinations eventually become entirely dissociated; at very high temperatures the only action possible is destruction of compounds. The medium realized at such temperatures, instead of being very complex, will be composed entirely of elements in the atomic state.

We have, however, to examine the role played by a strong compression. The latter will plainly accelerate reactions which are accompanied by a contraction in volume—which is to say, reactions between atomic bases. It is then seen to operate in inverse sense to increase of temperature, and if sufficiently strong makes possible, even at very high temperatures, the existence in molecular form of elements or compounds. To fix the ideas as to the magnitude of pressures capable of compensating the effects of certain high temperatures, we give several dissociation coefficients for hydrogen.

Temperature.	Pressure.	Dissociation Coefficient.
Degrees.	Atmospheres.	
3,000	1	6
4,000	1	25
5,000	1	92
6,000	1	99
6,000	10	80
6,000	100	53
6,000	1,000	19
6,000	100,000	2

These values are obtained, not by direct experiment, but by substitution in a well-known formula connecting molecular dissociation, temperature, pressure and heat of formation. Naturally it is not to be demanded of an expression of this sort, verified for very limited intervals of temperature and pressure, that it shall express with precision results for the extreme conditions called for by our problem. Nevertheless, the form of this equation rests upon the principles of thermodynamics, and it seems permissible to use it for obtaining at least a first idea as to the relative influence of the temperature and pressure factors, more especially in the case of hydrogen, which follows particularly well the empiric laws of perfect gases.

At 6,000 degrees and pressures below 100,000 atmospheres, hydrogen is found in a form almost entirely molecular, and if it obeys the same general rule up to the pressures and temperatures of the interior of the sun, its dissociation there cannot greatly exceed 10 per cent. Without insisting upon further numerical determinations, always a matter of great caution, we may conclude that at the interior of the sun, by virtue of the extreme pressure, the existence of complex systems, comprising alike atoms and molecules of both elements and compounds, may be considered possible. But there is no reason to suppose the medium thus obtained to comprise endothermic compounds to any great extent. We remark in this connection that the only compounds which Arrhenius claims to have identified in the depths of the sun-spots are magnesium and calcium hydrides and titanium oxide—all exothermic even at ordinary conditions.

On these grounds it may be concluded that a theory founded solely upon the destruction of endothermic substances accumulated in great masses at the center of the sun does not explain, in a way to conform with actual experience, the problem of the origin of the solar radiation.

All these considerations lead us to seek the participation in the solar radiation of chemical phenomena in the form, not of destruction of endothermic compounds, but of synthesis of molecules or compounds. Again placing ourselves, in this search, on the plane of practical experience, it is permissible, by reason of the elevated temperatures and pressures there ruling, to compare the interior of the sun to a more or less complex system of atoms and molecules in chemical equilibrium. In such a system, every loss of heat would be followed by a displacement of equilibrium, with formation of molecules from some of the atoms—reactions far richer in energy than the reduction to molecules of endothermic compounds. In support of this analogy we have the presence in the sun of many of the substances, which we know in the earth. In fact, in addition to coronium, a substance peculiar to the corona of the sun, the major part of the terrestrial elements is represented in the solar globe; and in particular, the existence of oxygen, basis of so many highly exothermic compounds, cannot be questioned. We may also recall, in this connection, the identification in the solar spots of such substances as metallic hydrides and oxides, exothermic even at ordinary temperatures and pressures.

The mechanism of chemical phenomena caused by refrigeration involves a gradual liberation of energy which would very well explain the continuity and regularity of the solar radiation. It remains to inquire whether the quantity of heat available from the operation of such reactions would be sufficient to account for the persistence of the radiation through the long geologic ages.

We have already indicated that a block of carbon of mass equal to the sun's could by its combustion support the solar emission of energy for a period of only five thousand years, at most. These figures, it is true, pertain to a reaction between molecules, of which the thermal value is much lower than that of a reaction between atoms. The latter thermal value, never heretofore available, can now be calculated with the aid of recent data, already cited, bearing upon the dissociation of element molecules. We append the results of such calculation for several compounds.

	Heat of Formation	
	From Molecules.	From Atoms.
	Calories.	Calories.
Hydrochloric Acid.....	22,000	144,000
Hydrobromic Acid.....	12,400	106,000
Hydroiodic Acid.....	0,450	85,000
Ammonia.....	12,000	250,000
Nitric Oxide.....	—21,000	150,000
Ozone.....	—30,000	200,000
Molecular Hydrogen.....	0	90,000

According to this table, while the figures pertaining to reactions between atoms are vastly superior to those pertaining to molecular formation, which we have been accustomed to find in the thermo-chemical tables, they are still infinitely too small to meet the exigencies of our problem. Of all chemical systems imaginable, one consisting of free atoms of hydrogen seems to contain the most latent energy, 45,000 calories per gramme as compared with 1,500 calories for nitroglycerine. The potential energy of such a system will exceed that of the system of carbon and oxygen already mentioned by little more than twenty times. But estimating as the length of duration of the solar radiations a period of one billion years—which is without doubt a minimum—it would be necessary, for the support of that radiation, that the potential energy in one gramme of the sun's matter should be two billion calories, close to fifty thousand times that contained in a gramme of atomic hydrogen. The discrepancy is too painful; we may state without reserve that no manifestation of chemical affinity of any sort actually known involves an emission of energy even remotely approaching the required magnitude.

We find ourselves as a consequence reduced to penetrating the domain of hypothesis in the search of a purely chemical theory. And there, in default of an explanation founded upon precise data, the considerations here adduced furnish us at least with a basis of orientation. This consists in supposing, as is alike possible and probable, that the atom is not the last step in the process of molecular dissociation. The quantities of energy put to work by this dissociation are naturally the stronger, the greater the temperature at which it is effected—just as the heats of reactions between atoms are greater than those characterizing action between molecules, which alone are susceptible to our usual processes of direct measurement. It is possible thus to imagine, for two simple bodies X and Y, and starting from the respective elements of dissociation of their molecules (from their proto-atoms, as we may call them)

a complete series of endothermic reactions leading to the substances X, Y, and finally to the compound XY.

The interior of the sun, if it consists of these proto-atoms, would afford a reservoir of energy accumulated in chemical form and disengaged gradually at the necessary rate. From the quantitative view, it would be necessary, we recall here, that the thermal value of reactions from proto-atomic bases be fifty thousand times greater than that of any known chemical reaction. It would be necessary that a gramme of matter, in the proto-atomic state, contain a reserve of energy of billions of calories. Such figures, which would have appeared inadmissible a few years ago by reason of their magnitude, create less consternation now that we know the fabulous amounts of energy set free during the atomic disintegration of the radio-active elements. Under this last form, it seems indeed that chemical phenomena might be able to participate to no mean degree in the maintenance of the solar radiation.

The Process of Wine "Chaptalization"

THE process of neutralizing the acid in wine by the addition of calcium carbonate has long been known in France by the term chaptalization. The term as well as the custom has made its way in Germany because of its convenience, and both name and practice have been legally authorized. The poor harvests of recent years have led to the extension of the practice, so that a German chemist, Dr. Theodore Paul, has considered it advisable to make a thorough study of the chemical reactions involved in the process, with a view of replacing previous empirical methods by those of scientific exactitude. He reports the result of his studies in *Die Umschau*.

The process consists in the addition to must or young wine of pure precipitated calcium carbonate; marble dust is also used in France. It has heretofore been supposed that because of this addition an equivalent neutralization of the wine took place, by means of the transformation of a corresponding portion of the free and half combined acids into calcium salts, the carbon dioxide formed at the same time escaping. Dr. Paul, finds the process to be more complex in its reactions, saying:

There is, in fact, in this neutralization a retrogression of the titratable acid corresponding in degree to the amount of calcium carbonate added. As demonstrated however by the researches previously undertaken by Th. Paul and Ad. Gunther, the degree of acidity of the wine is identical with the concentration of the therein contained hydrogen ions, and is dependent upon the equilibrium of the salts and acids contained in the wine.

Consequently the "de-acidification" of the wine with calcium carbonate is no simple neutralization process, but is the result of a series of chemical processes and alterations of equilibrium. To obtain a clear knowledge of this matter was the object of the present very extensive investigations, wherein I had the grateful aid of my assistant, Dr. Heinrich Zirkel. It was first determined that the precipitate formed in the wine after the adding of calcium carbonate consists essentially of neutral calcium acetate. Hence the study of this salt was the starting point of the research.

The next step was the experimental study of the chemical equilibrium between acetic acid and calcium carbonate in aqueous solution and in weak alcoholic-aqueous solution, and the application to the wine of the knowledge thus gained. In spite of the manifold variety of the chemical processes involved, the chemical equilibria can quite readily be represented schematically and can also generally be controlled by calculation.

The experiments show, among other things, that in the neutralization of an acetic acid solution with calcium carbonate the degree of acidity diminishes at the beginning with much more rapidity than it does later. This is due to the formation of primary and of secondary acetic acid ions, which remain in the solution until the formation of the precipitate of calcium tartrate, and exert their retarding influence on the dissociation of the acetic acid.

The titrimetric acid content of the solution on the other hand diminishes steadily and in direct proportion to the increase of calcium tartrate, as was theoretically predictable, and could be proved by continued titrations.

Finally there was undertaken a gradual neutralization of wines of pure nature, in accordance with these investigations. Here likewise there was exhibited a similar accelerated decrease in acidity at the beginning, having an unmistakable connection with the formation of the precipitate. The same thing was observed in gross by Von der Heide and Baragiola.

In consequence of the alcohol content, which diminishes the solubility of the calcium tartrate, this separation out begins earlier, and on this account the retardation of the hydrogen dissociation in the wine is not so noticeable at first, and the fall of the acidity curve is not so steep a descent as in the aqueous acetic acid solution.