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ART. XXXIV.—*The Solution of Vulcanized India Rubber;* by CARL BARUS.

1. INTRODUCTORY.—In my work* on the solubility of glass in water, I showed that in proportion as the state of dissociation or the molecular instability of glass is increased with rise of temperature, the solvent action of water increases at an enormously rapid rate; that inasmuch as the solution takes place between a solid and a liquid, sufficient pressure must be applied to keep the fluid in the liquid state, whenever the vapor tension at the temperature in question exceeds the atmospheric pressure. Thus, at 100°, the action of liquid water on glass is nearly negligible; but even at 185° solution occurs at so rapid a rate that capillary tubes may become filled with solid hydrated silicate, in place of water, in an hour. Here, however, about 10 atm. must be applied to keep the solvent in the liquid state essential to speedy reaction.

2. *The present application.*—Having attempted to apply the same principle to the actual solution of vulcanized India rubber, I obtained confirmatory results at once. To my knowledge this material has not heretofore been advantageously dissolved in a volatile reagent, or in any reagent by which it is speedily and copiously taken into solution, and from which it may be conveniently obtained. Cf. § 4, note.

It follows by analogy from § 1, that the rubber must be hot enough to be in a state of dissociation, i. e., that the coherence of the rubber-sulphur molecules must show an instability in regard to whatever solvent may be used. It follows, more-

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* This Jour., xxxviii, p. 408, 1889. Ibid, xli, p. 110, 1891.

over, that the system of rubber and solvent is to be kept under pressure sufficient to insure the liquid state of the solvent. It follows obviously that this temperature must only be so high, cæt. par., as to change in the least degree possible, the useful character of the rubber eventually to be deposited from solution. Hence, I act on vulcanized India rubber at the lowest convenient temperature facilitating the solvent action, and at a pressure preferably exceeding the vapor tension of the solvent at the given temperature. Whatever other favorable action pressure may exert (such, for instance, of forcing the fluid into the physical pores of the semi-solid by a principle akin to Henry's law) is clear gain. In my machine* it is rather more convenient to act under 100 atm., or more, than at lower pressures. Hence I did not scruple to use pressures as large as, or above, this, testing the adequacy of low pressures, however, by special experiment. §§ 18, 20.

The samples of vulcanized rubber acted on were five in number, and their character may be detailed as follows:

a. Very elastic† sheet rubber, usually not pigmented, translucent in thin films, brownish in color, used for rubber bands and sheeting, chemical rubber tubing, etc.

b. Less elastic and harder rubber, pigmented gray, opaque, largely used for rubber tubing, etc.

c. Non-elastic, pigmented rubber, flexible, opaque gray, used for low class rubber tubing and low class merchandise in general.

d. Ebonite.

e. Same as *a*, rotted by age and exposure.

3. *Solution in carbon disulphide.*—From experiments made at 100° and 160°, it appears that elastic sheet rubber (*a*), is not fully soluble in CS_2 in a reasonable time, if at all. It is quite soluble at 185°, and soluble to a remarkable degree and at a remarkably rapid rate at 210°. Hence the pressure under which solution is to take place, should here be greater than

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* See Proc. Am. Acad., xxv, p. 93, 1890, or Phil. Mag., October, 1890, p. 338. The present method of work is simple: Glass tubes 10^{cm} to 15^{cm} long, and $\cdot3^{cm}$ or $\cdot4^{cm}$ in diameter, closed at one end, and drawn out to a capillary canal with three enlargements at the other, were filled with a charge of vulcanized rubber and solvent, and then introduced into the steel piezometer tube. I made use of the temperatures of boiling turpentine (160°), aniline (185°), naphthalene (210°), and diphenylamine (310°). To separate the charge from the oil of the piezometer which transmits pressure, I first employed a thread of mercury inserted into the capillary canal. Finding, however, § 17, that this metal acted on the charge, I replaced it by a thread of water, or contiguous threads of gasolene and water. Charges were usually introduced in the ratio of one part by volume of rubber to three or more of solvent, § 18. About 1^{cc} to 2^{cc} of solution were obtained per heating. I made considerably over 150 experiments, most of them at 210° and 100 or 200 atm. Experiments on a larger scale were also made in great number, chiefly with the object of studying the product deposited from solution. § 20.

† By elastic I mean extensible with resumption of the original shape when the pull ceases.

15 atm., but need not exceed 30 or 40 atm. Inasmuch as CS_2 thus unites with rubber in any proportions, clear brown solutions of any viscosity may be obtained. Diluting such (thick) solutions with cold CS_2, the solvent is first greedily absorbed; but the final complete solution of the unagitated syrupy rubber takes places very slowly. Finally, by exposing any of the solutions to air, the CS_2 evaporates, and the dissolved vulcanized rubber is regained without sacrifice of its original non-viscid quality. Similarly fissured brittle sheet rubber or tubing (*e*), which has become useless for practical purposes by age, is quite soluble in CS_2 at 200°, so far at least as its undecomposed portion is concerned. Elastic gray rubber (*b*), dissolves completely to a gray liquid, in which the pigment is suspended. § 16. The concentrated solution hardens at once on exposure to air, reproducing a rubber of nearly the qualities (*b*). The same is true of the non-elastic sample (*c*). Treatment at 310° resulted in a decomposition of the rubber.

Commercial ebonite (*d*) is first partially devulcanized at 200°, (excess of rubber) and eventually dissolves in excess of solvent. The partially devulcanized product is elastic on drying, but finally hardens to a tough solid having a leathery quality. The solution leaves a black stain, with free sulphur apparent after evaporation. § 15. Gases are frequently evolved during solution of highly vulcanized rubber in CS_2. §§ 17 and 19.

As a whole my experiments show that excess of sulphur is first removed by the solvent, after which the vulcanized rubber itself passes into solution. § 15.

4. *Solution in liquids of the paraffine series.*—The elastic rubbers (*a* and *e*) dissolve easily in liquid mineral oils, at 200°. The pressure necessary will, of course, vary with the boiling point of the oil used, and may be as high as 50 atm. in the very volatile gasolenes. Commercial gasolene, though a good solvent of the rubbers *a* and *e*, is less powerful in case of *b* and *c*, unless excess of solvent be used. On exposure to air, the gasolene evaporates, leaving a residue which soon hardens. Mineral oils of a higher carbon order than gasolene, petroleum,* for instance, dissolves the rubbers *a* and *e* even more easily. The solution, however, dries only after much time and probably only in thin films. Solubility seems to increase as the oil lies higher in the carbon series. §§ 12, 18.

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* Looking up the literature of the subject, I found that John J. Montgomery (Cf. Letters Patent No. 308,189, November, 1884, U. S. Patent Office), describes a process for the solution of vulcanized rubber. His statement of the temperature and pressure necessary are substantially correct, although he confines his experiments to a petroleum oil boiling at 200° or higher. The oil is subsequently driven off by injections of steam. This is the nearest approach to an available and true solution (a solution which does not remain permanently sticky like the turpentine and other solutions) which I have found. The essential peculiarity of the methods in the above text is solution in volatile solvents.

5. *Solution in turpentine.*—In case of the elastic rubber (*a*), complete solution is at once effected at 200°, whereas at ordinary temperatures the time necessary is enormous, if indeed the solutions in the two cases be the same. The syrupy liquid obtained at 200° seems to dry in very thin films. Special experiments made at 160° showed that no reasonably speedy solution takes place even in liquid turpentine at this temperature, thus corroborating the inferences of §§ 1, 2, 3. Gray rubber (*b*) is acted on with greater difficulty at 210°. The solution leaves a white glossy stain which hardens. Pressure need not exceed 5 atm.

6. *Solution in chloroform and carbon tetrachloride.*—Elastic sheet rubber (*a*) dissolves at once in liquid $CHCl_3$ at 210°. Pressure should exceed 15 atm. and need not be larger than 25 or 30 atm. Solutions of any degree of viscosity seem to be obtainable. They dry at once on exposure to air, leaving a hard residue relatively dark in color. Possibly this was due to the presence of sulphur in the chloroform. § 15. Gray rubber (*b*) is attacked with decomposition of the solvent and evolution of gas.

7. *Solution in aniline.*—Solution in the liquid at 200° takes place at once, in case of elastic rubbers (*a*). Pressure need not exceed a few atmospheres. Thin films apparently dry on long exposure.

8. *Solution in animal oils.*—Neither in the case of sperm oil, nor of lard oil was the elastic rubber (*a*) dissolved on removing from the piezometer. Both distintegrated on standing, to a solution, often with slow evolution of gas.

9. *Treatment with glycerin.*—At 200° no solution occurs. Glycolic alcohols were not examined. Cf. § 12.

10. *Solution in benzol and higher aromatic hydrocarbons.*—The elastic sheet rubber (*a*) dissolves at once in liquid C_6H_6 at 200°. Pressure should exceed 7 atmospheres, but need never be higher than 30 atm. The solution exposed to air hardens rapidly. Solution of gray rubber (*b*) is less easy.

Solution of elastic rubber (*a*) in liquid toluol at 200° also takes place with great ease. The liquid dries slowly. Pressures of less than 10 atm. suffice.

11. *Solution in ethylic and higher ethers.*—Elastic sheet rubber (*a*) dissolves at once in liquid ethylic ether at 200°. Pressure should exceed 25 atm., but need not be greater than 40 or 50 atm. The solution hardens immediately on exposure to air. Gray rubber (*b*) is attacked with difficulty.

12. *Treatment with alcohols.*—At 200° india rubber (*a*) is not dissolved in liquid methyl or in liquid ethyl alcohol, and only slightly so in liquid amyl alcohol. Thus, again the solubility seems to increase with the molecular weight of the solvent. § 18.

13. *Treatment with ketones.*—India rubber (*a*) treated with liquid acetone at 200°, is converted into a sticky paste from which it hardens at once on exposure to air. Pressure should exceed 15 atm., but need not be greater than 30 or 40 atm.

14. *Treatment with water and mineral acids.*—In no case was there a trace of true solution at 210°. Water probably enters the physical pores of the elastic rubber (*a*), as this substance becomes superficially rough and warty on drying in steam at 200°, after being treated with liquid water at the same temperature. It does not melt. § 18. Strong hydrochloric acid (1 : 2) has no obvious effect, while strong sulphuric acid (1 : 3) seems only to char the rubber. Treating gray rubber (*b*), with HCl, I found its solubility in CS_2, C_6H_6 and gasolene to have decreased.

15. *Treatment for vulcanization. Liquid ebonite.*—Liquid ammonic polysulphide at 185° or 200° does not change the appearance of gray rubber (*b*) markedly; but the sample loses its elasticity and shows a semi-plastic consistency. This I believe to be due to additional vulcanization induced by the polysulphide. If now the sample be treated with liquid CS_2 at 200°, the solvent is decomposed with the evolution of much gas, and the rubber restored to its original elastic quality. The gas is liberated throughout the mass of the rubber, and the sample, when taken out of the tube, has the form of an enormously inflated cellular sack, which issues from the glass tube explosively, but soon collapses on exposure to air. As a whole these results agree with the behavior found for ebonite in § 3. In both cases it is possible to pass from a more vulcanized to a less vulcanized solvent by treating an excess of rubber. It will be shown below, § 19, that the gas evolved is probably due to the double decomposition of water and CS_2.

More interesting is the direct vulcanization of a rubber solution, to liquid ebonite, by aid of a solution of sulphur. In case of elastic sheet rubber (*a*), this even begins at 160°; but it is more complete at 185° and 210°. In case of pure (non-vulcanized) rubber dissolved in CS_2 with excess of sulphur, scarcely any change of the flesh color is observed at 160°, and the sulphur crystallizes out of the solvent in needles, on exposure. At 185° and 210°, however, the charge turns black, showing complete vulcanization. If equal masses of vulcanized rubber (*a*) and sulphur be treated, the product, after heating to 210°, is not dissolved nor soluble, until the excess of sulphur is removed. §§ 3, 15. Gas is often evolved. §§ 17, 19. In proportion as less sulphur is used relatively to the rubber, the product becomes more immediately soluble and less gas is evolved. Adding about 20 per cent of dissolved sulphur to the elastic rubber (*a*), I obtained serviceable solutions of ebonite, on treating at 200° either in CS_2 alone, or in mixtures, § 16, of this liquid with gasolene, benzol, etc. In most cases these harden very quickly to a jet-black enamel. With less sulphur the color is brown in thin films.

16. *Solution in mixtures of solvents, and solution of mixed gums.*—By acting on vulcanized rubbers with mixed solvents of the above kind, I obtained very satisfactory results. All the rubbers mentioned (*a* to *e*), ebonite excepted, pass easily into true solution by such treatment. Thus the gray elastic rubber (*b*) dissolves at once in a mixture of CS_2 with gasolene, or benzol, or ether, etc.; or of benzol and toluol; or less easily in mixtures of benzol and gasolene; etc. Ebonite is partially devulcanized, and would probably be dissolved in large excess of solvent. § 3. No gas was evolved in any case, § 19, which is an advantage of this method. In all cases the solutions hardened rapidly on exposure to air, yielding the pigmented rubber if the solution be shaken, or a purer rubber, if the sediment be removed by subsidence and decantation.

Equally feasible is the solution of mixed gums in a suitable solvent at 200°. Thus I made solutions of mixed vulcanized rubber and gutta percha in CS_2, which dried at once on exposure to air; mixtures of rubber and shellac dissolved in CS_2, drying more slowly; mixtures of vulcanized rubber and rosin dissolved in CS_2 and in gasolene, which dried in thin films only after long exposure; etc.

17. *Direct devulcanization.*—When, by any of the above methods a solution of vulcanized rubber is obtainable, direct devulcanization may be attempted by mixing the charge with some sulphur absorbent. Such material must be chosen which at 200° acts neither on the rubber nor the solvent. Metallic filings do not appear to be available. Treating ebonite with CS_2, C_6H_6, or gasolene, to which copper filings had been added, I found the charge, after exposing to 200°, to be disintegrated, while an enormous amount of gas was evolved. Scarcely any of the solvent was left in the tube. The direct action of copper or of sulphur, on CS_2, etc., at 200° is insufficient to account for this reaction. § 19. The gas must, therefore, be produced at the expense of the ebonite, or of the reagent in presence of ebonite; and since all the solvents used behave alike, at the expense of the ebonite. This may furnish some clue as to the chemical character of the rubber as related to the gases evolved. Gaseous decomposition frequently sets in on exposure of highly vulcanized rubber solutions even to ordinary room temperatures, whereas at 0° and under slight pressure (1 or 2 atm.) the gas remains in combination. Bright steel is

scarcely attacked.* In fusing impregnated india rubber, § 18 I frequently noticed that the colder ends of the mass were opaquely discolored. Possibly, therefore, the sulphur at 200° may be gradually segregated by diffusion or evaporation. My experiments on this subject failed.

18. *Fusion of impregnated rubber.*—If vulcanized india rubber be impregnated or saturated by digesting it with the cold reagent (any solvent of pure rubber), for a suitable time (a few minutes to many hours), the swelled mass not only shows a relatively low melting point, but it remains liquid after cooling, provided the solvent is not allowed to escape. This is an observation of practical importance, since the retorts† can thus be charged with solid or dry rubber, a minimum of solvent be used in treating or lost by evaporation, and concentrated solutions be obtained often fit to be used at once. The rubber so melted hardens on exposure. Finally the pressure necessary in this case is the smallest possible, and may be below the data given for the divers solvents above.

The quantity of solvent retained by solid rubber is very large: Thus elastic sheet rubber will hold 7 or 8 times its weight of CS_2, or 1 to 2 times its weight of naphtha. Gray rubber (elastic) absorbs more than its weight of naphtha; etc.

Experiments may be cited as follows: Non-impregnated vulcanized rubbers (*a* to *e*) do not melt if exposed in a closed tube at 210°. Only in the case of very slightly vulcanized pure rubber gum is there a trace of fusion perceptible at the edges, and here it may even be due to a stain of dirt (oil) accidentally left there. Gray rubbers (*b*, *c*) with a superficial coating of exuded sulphur, turn black from the formation of a film of ebonite.

All the india rubbers (*a* to *e*) fuse at 210°, when previously saturated, or nearly so, with cold carbon disulphide, and exposed in a close-fitting glass tube. If the pressure be reduced by a capillary aperture at one end of the otherwise closed glass tube, or if the tube be only partially filled and the empty end kept cool, the impregnating solvent is merely distilled off, and no fusion takes place. Whereas at 160° fusion scarcely occurs, melting seems to be complete in the well impregnated elastic rubber (*a*) at 175°. There is therefore an approximate coincidence of the thermal data in the present and in the above paragraphs.

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* Fortunately, therefore, steel apparatus is available on a large scale. An interesting question occurs as to what becomes of the carbon, in the case where sodium, mercury, copper, etc., are attacked by hot liquid CS_2 and not by cold CS_2.

† The present experiments were made in *closed* glass tubes, nearly filled with the impregnated rubber. After fusion the mass frequently appeared to have shrunk. Cf. § 2.

Similar results were obtained with benzol, with gasolene and higher petroleum oils, etc. Fusion is absent or only incipient at 160°, and more than complete at 210°, provided the gasolene be not too volatile. §§ 4, 12. In general the gray rubbers (*b*, *c*) fuse to a more viscous mass than the gum rubbers (*a*), the consistency of cold solutions in the latter case about that of treacle.

The occurrences of this paragraph therefore would resemble the fusion of a salt in its water of crystallization, but for the exceptional behavior that impregnated vulcanized rubber after fusion retains a consistency which is liquid relatively to the original non-impregnated charge. The analogy with the solution of starch, or of gluten, is thus more close and immediate. In all these cases the solid swells up when impregnated with the solvent, and fuses to a relatively less viscous consistency, or to a thin solution, when a certain temperature (below 100° in case of starch and gluten and above 160° in case of vulcanized india rubber) has been reached. Hence it is not unreasonable to suspect that even ordinary dry wood, or woody tissue, which swells to a marked degree when impregnated with water, may pass into actual solution if the temperature at which the water acts is sufficiently high, and the pressure above the vapor tension of water at that temperature.*

I mention finally that the reduction of melting point produced in vulcanized india rubber by the impregnating reagents may perhaps advantageously be discussed in accordance with Raoult's law; but owing to the difficulty of defining the melting point of the unimpregnated rubber, and the close proximity of the melting points after impregnation with different reagents (CS_2, C_6H_6, gasolene) my views on this subject have not taken shape. It is known that in general that the melting point produced by a dissolved colloid is relatively very small, from which an exceedingly large molecular weight of the colloid has been inferred. The above results show that in the converse experiment, where the melting point of the colloid is lowered by a solvent, the effects will probably be normal and pronounced.

Nevertheless I doubt whether the thin rubber fluids obtained are true solutions, i. e. represent a case in which the division of the solid has actually reached a definite molecule; for on

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* I have since tested this surmise at some length, but found in every case that cellulose is decomposed before solution in water takes place. In spite of the presence of water under pressure, the phenomenon seems to be a dry distillation. I may here refer to the remarkably close analogies in the thermal behavior of rubber and gelatine which have recently been discovered by Bjerken (Wied. Ann., xliii, p. 817, 1891). The author has reason to believe that moist gelatines are heterogeneous mixtures of solid and liquid. The behavior of rubber, as discussed above, is characterized at low temperatures by a fixed maximum of absorbed solvent. The term mixture is scarcely applicable at once.

long standing in sealed vessels a gradual thickening of the liquid with final coagulation seems to be the invariable result. Thus there must be a gradual growing together of the individual particles, until finally the whole solution forms one coherent gelatinous mass.

To summarize: Suppose the coherence of rubber to be due to (cohesive) affinities, capable of being saturated like ordinary affinities. Then in case of impregnation with a solvent, a part of these combine with the similar affinities of the solvent. The result is the decided decrease of tenacity (observed). To liquefy the impregnated sample, the residual cohesive forces of the rubber must be withdrawn, and this can be done by heat. The liquid so obtained, I do not conceive to be a true solution, but rather a suspension of particles, the exceeding fineness of which is determined by conditions discussed elsewhere.* Diffusion is thus an excessively slow process, and hence the liquid on cooling need not become solid again. In proportion as the individual particles unite however, coagulation gradually sets in, and its structure is probably that of a fine sponge holding solvent in its interstices. If the coagulated solution be reheated (under pressure), a thin viscid solution is again obtained, which in its turn coagulates.

19. *Behavior of reagents.*—The frequent occurrence of gaseous products in the above experiments made special experiments on the decomposition of reagents necessary. Benzol and gasolene were found stable at 210°, and often above this temperature, both in the presence of water, or of sulphur. §21. Carbon disulphide, however, in addition to relatively slight decompositions producible by sodium, or mercury, or copper (§17), at 210°, is doubly decomposed by water at this temperature, with the evolution of much gas, presumably H_2S and CO_2. CS_2 remains stable in the presence of zinc white (a common rubber pigment), or of sulphur, or of bright steel, at 210°. §17. Hence a thread of mercury to shut off the experimental tubes, §2, is generally objectionable, as is also a thread of water in case of CS_2. Moreover the absence of gaseous reaction in case of mixed solvents, §16, is to be attributed to the fact that CS_2 and the water are intentionally separated by layers of benzol or gasolene.

An interesting question is suggested here, as to whether it be possible to express affinity on a scale of temperatures. Let it be required to determine the affinity of a metal for sulphur. At ordinary temperatures not even sodium decomposes CS_2, whereas such decomposition occurs if the temperature be sufficiently high. Hence the temperature at which the decomposition definitely sets in (for copper sooner than for iron, etc.) is

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* Barus: this Journal, xxxvii. pp. 126–128, 1889.

a reciprocal expression of the affinity of the given metal for sulphur,—bearing always in mind that the stability of the solid metallic molecule also enters into the consideration. The arbitrary reagent CS_2, in its relations to all the metals to be examined, fulfills a similar purpose to an arbitrary spring balance in measuring gravitational forces. § 21.

20. *Summary of the results.*—In the above paragraphs I have therefore indicated a method by which vulcanized india rubber of any quality or character whatever, as well as the undecomposed or reclaimable part of rubber waste, may be dissolved or liquified in a reasonably short time;* the solutions possessing any desirable degree of viscosity or diluteness, from which india rubber may be regained on evaporation of the solvent.

I shall elsewhere describe divers forms of apparatus by which the above operations may be carried out on a larger scale. They are of no interest here; but I mention them since it is only from such work that a full insight into the quality of the rubber deposited from any given solution may be obtained. Experiments made in bulk in this way showed the material deposited from solution to be considerably inferior to the original rubber, both as regards tenacity and elasticity. Its chief value in the physical laboratory will therefore be that of furnishing an air-tight cement or an acid-proof varnish, capable of withstanding more than 200° centigrade. Rubber newly deposited from any of the above solutions presents a very curious case of slowly reacting elasticity. If a thread, say 0·1 cm. thick, be twisted and then let go on a frictionless surface, it will squirm like a live worm for some minutes. If it be stretched, the original length is regained with visible slowness.

Throughout my work the approximate constancy of the dissolution temperature irrespective of the solvent has been the marked feature. Thus in case of CS_2, of turpentine, of the vulcanization of dissolved pure india rubber, etc., no action took place below 160°. Even this temperature is higher than is needful for vulcanization effected in the dry way, where 110° to 140° are deemed sufficient. Moreover the solution of vulcanized rubber in CS_2, for instance, takes place quite as easily under 700 atm. as under, say 20 atm., as is particularly manifest from the fusion of impregnated rubber, and in special high pressure experiments. In my work on the compressibility of liquids† I showed that compressibility is essentially associated with the extra-molecular forces whereas the molecule remains relatively incompressible. Temperature, however, has immediate access to the molecule; and thus it follows that

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* Practically at once, if the material is not too bulky.

† This Journal, xxxix, p. 510, 1890.

whereas the effect of temperature in experiments like the above is manifest, the effect of pressures of the order applied is relatively inappreciable.

21. *Digression.*—From the above paragraphs I infer that the difficulty encountered in endeavoring to dissolve carbon is probably attributable to a relatively high dissociation temperature of the solid carbon molecule. I made many experiments to test this view, in all of which I failed to obtain solution even at low red heat and 600 atm. of pressure. My work thus corroborates the negative results of Hannay* on the direct solution of carbon. My tests were made with gasolene, water, benzol and carbon disulphide, usually at 500° and 500 atm. In case of gasolene I observed at higher temperatures. Usually the reagents were decomposed (particularly CS_2, C_6H_6 and $CHCl_3$) with the evolution of much gas, while the carbon remained appreciably unaffected. Decomposition by metals (copper corroded by CS_2, and gasolene acted on by palladium) showed sooty deposits only.