and $(NH_4)_2SO_4$ and it is evident that two cases may occur. It may be that the two liquids contain the two components in the same proportion as they occur in the double salt; it is then as if the double salt dissolves in both liquids without decomposition. If this is the case the liquids c_1 and c_2 will be in equilibrium with each other.

The second possibility is that one of the liquids has in regard to the double salt an excess of Li_2SO_4 and the other, therefore, an excess of $(NH_4)_2SO_4$; in this case, c_1 and c_2 cannot be in equilibrium with each other. The experiment now shows such to be the case. When I saturated a water-alcohol mixture with $LiNH_4SO_4$ at $50°$, the alcoholic layer contained a small excess of Li_2SO_4 and the aqueous layer a small excess of $(NH_4)_2SO_4$. From this it follows that the conjugation line does not coincide with the surface DAW but intersects it; the part to the right of the line must be situated in front of the plane and the left part behind it. The alcoholic solution c_2 of the double salt cannot, therefore, be in equilibrium with the aqueous solution c_1 of this double salt, but may be so with a solution containing an excess of $(NH_4)_2SO_4$.

Chemistry. *"On catalytic reactions connected with the transformation of yellow phosphorus into the red modification."* By Dr. J. Böeseken. (Communicated by Prof. A. F. Holleman).

(Communicated in the meeting of January 26, 1907).

I.

From the researches of Hittorf (Pogg. Ann. 126 pag. 193) Lemoine (Ann. Ch. Ph. [4] 24. 129) Troost and Hautefeuille (Ann. Ch. Ph. [5] 2 pag. 153), R. Schenck (B. Ch. G. 1902 p. 351 and 1903 p. 970) and the treatises of Naumann (B. Ch. G. 187 2p. 646), Schaum (Lieb. Ann. 1898. 300 p. 221), Wegscheider and Kaufler (Cent. Blatt 1901 I p. 1035) and Roozeboom (Das heterogene Gleichgewicht I p. 171 and 177) it appears highly probable that red phosphorus is a polymer of the yellow variety, which polymerism is, however, restricted exclusively to the liquid and the solid conditions: the vapour (below $1000°$) always consists of the monomer P_4.

From the above considerations it moreover follows that the yellow phosphorus is metastable at all temperatures below the melting point of the red phosphorus ($630°$); it may, therefore, be expected that it will endeavour to pass into the red variety below $630°$.

Although there are many instances where a similar transformation, as with phosphorus at a low temperature, proceeds exceedingly slowly, the velocity in this case is certainly strikingly small. Even at 200°, when the metastable substance possesses a considerable vapour tension, it is still immeasurably small even though red phosphorus may be present. [1]) This extraordinary slowness, notwithstanding the considerable heat quantities liberated during the transformation, and the complete alteration of properties caused thereby, have a long time since established the conviction that the two modifications of phosphorus are each other's polymers and that the red one has a much more complex molecule than the yellow one, but the real cause of that slowness is not elucidated thereby.

As regards the question *how* this condensation takes place, Schenck (l.c.) was the first to endeavour to answer this experimentally. On boiling yellow phosphorus with an excess of PBr_3, he succeeded in changing it to the red modification at 172° with measurable velocity; and from his first investigations he concluded that the order of this reaction was a bimolecular one:

$$2\,P_4 \rightarrow P_8.$$
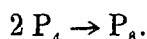
This was meant to represent the first phase, for Schenck pointed out that red phosphorus had no doubt a higher molecular weight than P_8, which subsequent condensation should then take place with great velocity; in other words he arrived at the rather improbable result that the condensation of P_8 to P_n would take place much more rapidly than that of the simple P_4 molecules to P_8.

At a repetition of these measurements with one of his pupils (E. Buck), they came indeed to the conclusion that the reaction is monomolecular (B. Ch. G. 1903 p. 5208). He remarks "Daraus geht mit Sicherheit hervor, dass die Reaction der Umwandlung des weissen Phosphors in rothen monomolekular verläuft." .

He, however, adds "Daraus könnte man den Schluss ziehen, dass die Molekular-gewichte des weissen und rothen Phosphors identisch sind."

It strikes me that Schenck arrives here at a less happy conclusion. From ' the occurrence of a mono-molecular reaction we need not necessarily come to the conclusion that the *entire* process proceeds in this manner.

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[1]) Roozeboom (l.c.) compares this to the retardation of the crystallisation of strongly undercooled fusions as 200° is more than 400° below the melting point of red phosphorus: I am, however, of opinion that this view is untenable on account of the relatively high temperature, and particularly the very great mobility of the yellow phosphorus (Roozeboom l.c. p. 89). The cause of the phenomena must be looked for elsewhere.

'On the contrary as in so many other chemical transformations, we must assume that the measurements executed only apply to a subdivision of the reaction, namely to that with the smallest velocity.

In this case it is only natural to suppose that the velocity determinations of SCHENCK and BUCK apply to the decomposition of the P_4 molecule [1]) into more simple fragments (P_2 of P), then at once condense to the red modification so that we may represent the whole process in this manner for instance:

$$P_4 \text{ (yellow)} \rightarrow 2P_2. \quad\quad\quad\quad (1)$$

$$nP_2 \quad\quad \rightarrow P_{2n} \quad\quad\quad\quad (2)$$

in which the reaction velocity of (2) is very much larger than that of (1).

(We might also suppose, as a primary reaction the transformation of the metastable phosphorus into a *labile* P_4; this, however, I do not think so probable because, in the determination of the vapour density above 1000°, a *splitting* has been indeed observed).

It cannot be a matter of surprise that this decomposition velocity at 200°, (without catalyst) will still be extremely small, looking at the great stability of P_4 in the state of vapour; and if this decomposition, as I suppose, must precede the condensation, the separation of the red phophorus at that temperature will proceed at least equally slowly.

There is also nothing very improbable in the very rapid transformation of the dissociated P_2 or P into red phosphorus.

The fact that the allotropic transformation takes place particularly under the influence of sunlight is certainly not in conflict with the idea of a primary splitting, as we know that the actinic rays accelerate the decompositions (such as of HJ, AgBr, C_2J_2, etc.).
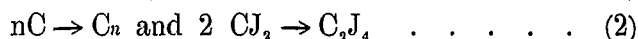
I wish also to point out that a primary splitting is also accepted in other monomolecular reactions, such as in the decomposition of AsH_3 (VAN 'T HOFF's Vorlesungen), of CO (SCHENCK B. Ch. G. 1903 p. 1231 and SMITS and WOLFF. (These Proc. 1902 p. 417). [2])

The monomolecular splitting of C_2J_2 into C and C_2J_2 SCHENK and

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[1]) Although the size of the molecule of the liquid yellow phosphorus is not known with certainty, the identity with that of the vapour is however very probable; for the rest it does not affect the argument.

[2]) I omit purposely the beautiful researches of M. BODENSTEIN, although for the union of S and H. he also arrives at the conclusion that a primary splitting of the S_8 molecule precedes the union with H_2, because we are dealing here with heterogeneous systems in which solubility velocities play an important rôle. It is not impossible, that in all cases in which *amorphous* substances separate we are dealing with such solubility velocities.

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Sitzendorff B. 1905, p. 3459, may be interpreted in the simplest manner by the succession of the reactions :

$$C_2 J_2 \rightarrow C + C J_2 \quad \ldots \ldots \ldots \ldots \quad (1)$$

$$nC \rightarrow C_n \text{ and } 2 \ C J_2 \rightarrow C_2 J_4 \quad \ldots \ldots \quad (2)$$

II.

The measurements of Schenck and Buck have been made at the boiling point of PBr_3. As this is situated at 172°, it appears that the solvent exerts a considerable accelerating influence on the transformation, as pure yellow phosphorus at 200° remains practically unaltered.

The solvent, therefore, acts catalytically; a still more powerful influence has $AlCl_3$. If this is brought together with phosphorus in vacuum tubes, the transformation takes place even below 100°.

The catalyst is at once covered with a layer of pale red phosphorus, which it is rather difficult to remove by shaking, so that it is necessary to add now and then a fresh quantity of $AlCl_3$. The action proceeds much more regularly if benzene (and particularly PCl_3) is added as a solvent. At the boiling point of this, the transformation is completed after a few hours (respectively, minutes); the product is Schenck's scarlet-red phosphorus but much contaminated with benzene and condensation products, which are retained with great obstinacy.

In connection with the explanation in part I. I believe that the observations of Schenck and of myself throw some light on catalytic actions in general.

For it is very probable that in this allotropic transformation a splitting occurs first; we notice that the transformation, consequently the splitting, is accelerated by PBr_3 or $AlCl_3$. Will this not occur generally in catalysis ? As a dissociation precedes most reactions it is probable that this question must be answered in the affirmative. (I wish, however, to lay stress on the fact, that in answering this question we do not penetrate into the real nature of catalysis. The reason *why* the dissociation acceleration occurs, whether this is connected with a temporary combination of the catalyst with the active molecules, or whether the catalyst removes the cause which impedes the dissociation, remains unexplained and need not be discussed here any further.)

As far as I have been able to ascertain, this conception is not antagonistic to the facts observed; in fact a number of cases are known where a catalyst causes *directly* a splitting or considerably accelerates the same.

Platinum, for instance, powerfully accelerates the decomposition of hydrogen peroxide, ozone, nitric acid, hydrazine etc.

Aluminium chloride causes a direct splitting of the homologues of benzene, of the very stable polyhalogen derivatives, of aromatic ethers, of sulphuryl chloride, etc. The number of these decompositions is so considerable that, in other cases where we cannot prove a direct dissociation by the catalyst, we may still argue that it takes place primarily, or rather that an already present but exceedingly small dissociation is accelerated in such a manner that a system attains the stable condition of equilibrium much sooner than without the catalyst.

The great evolution of heat in the process

$$HCCl_3 + 3\ C_6H_6 + (AlCl_3) = (C_6H_5)_3\ CH + 3\ HCl + (AlCl_3)$$
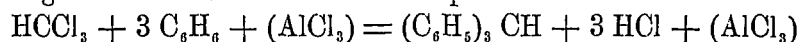
points to the fact that the system to the right is more stable than that to the left. I attribute its slow progress when no $AlCl_3$ is used to the small dissociation velocity of chloroform : the catalyst accelerates this dissociation so that the stable condition of equilibrium is attained in a short time. This reaction gets continuously more violent (the temperature being kept constant). This phenomenon may be readily explained if we bear in mind that the reaction proceeds in different stages ($C_6H_5\ CHCl_2$, $CHCl\ (C_6H_5)_2$ and $CH(C_6H_5)_3$ are formed in succession) and that the chlorinated intermediate products are decomposed much more readily than $CHCl_3$.

If sulphur is boiled with benzene and aluminium chloride we obtain almost exclusively $(C_6H_5)_2\ S$, $(C_6H_4)_2\ S_2$ and H_2S. Without the catalyst hardly any action takes place because the dissociation of S_8 in benzene solution at 80° is negligible : (if sulphur is boiled with toluene H_2S and condensation products are formed without $AlCl_3$ being present) the aluminium chloride accelerates the reaction $S_8 \rightarrow 4\ S_2$, and consequently the formation of the condensation products. This explanation is therefore quite the same as that given for the reaction of P_4 with benzene and aluminium chloride ; the sole difference is that in the latter the second stage of the reaction consists exclusively in the condensation of P_2 to red phosphorus, a condensation to which sulphur does not seem to be liable to the same extent, so that the dissociated sulphur forms with benzene the above products.

I consider the formation of a compound of the catalyst with one of the reacting substances of importance for the taking place of the reaction in so far only that one phase can be formed ; otherwise it rather obstructs the reaction, because the catalyst becomes to a certain extent paralysed. One of the most powerful catalysts, platinum, is actually characterised because it does *not* (or at least with great

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difficulty) unite with the reacting molecules, but forms a kind of solid solution. Carbon tetrachloride which forms no compound with aluminium chloride is certainly attacked by benzene in presence of that catalyst not less easily than benzoyl chloride which does form an additive product; whilst also the chlorine atom in the acid chloride is certainly not less "mobile" than that of CCl_4.

GUSTAVSON imagines that the formation of compounds, such as $C_6H_3 (C_2H_5)_3 Al_2Cl_6$ is necessary for the action of C_2H_5Cl on benzene; these were separated from the bottom liquid layer which forms during the action of C_2H_5Cl on benzene and aluminium chloride; if, however, the formation of this layer is prevented as much as possible, the yield of ethylated benzene improves. Therefore I do not call its formation *necessary*. That it may act favourably perhaps is because the catalyst and also the two reacting molecules are soluble in the same, thus allowing them to react on each other in concentrated solutions.

As has been observed above, there is something unsatisfactory in assuming intermediate reactions in order to explain catalytic phenomena. I will try to explain this matter more clearly.

As is known, we may express the reaction velocity of a condition change by the ratio: $\dfrac{\text{impelling force}}{\text{resistance}}$ in which the impelling force for that change in condition possesses a definite value which a catalyst cannot alter in the least; the resistance, however, is dependent on influences for the greater part unknown. Therefore, the resistance must be lessened by the catalyst and the question to be solved is: "On what does this decrease in resistance depend?"

If we suppose that intermediate reactions take place we divide the process into a series of others of which each one considered by itself is propelled by a force less impelling than the total change; the resistance of each of those division processes must, therefore, be much less, and the question then becomes: How is it that those intermediate reactions proceed much more rapidly than the main reaction? which is in fact nothing else but a circumlocution of the first question: how is it that the catalyst decreases the original resistance? Therefore, by assuming intermediate products, we have not been much enlightened, on the contrary we have made the problem more intricate, because, instead of having to account for a single increase of velocity, we have to look for that of at least two.

I call to mind the theory of OSTWALD who supposes each process to be a succession of condition changes, which will be all possible if they occur with potential diminution. If, however, the first of those

changes can commence only with absorption of free energy, the process will not take place unless a catalyst is added; this, therefore, opens another road . . . Now, in my opinion too much attention is paid to the milestones on that road and too little to the opening itself.

This is chiefly caused by the fact that we know so little of the so-called „passive resistances", for instance we cannot give a satisfactory explanation of the fact that iodine acts much more rapidly at low temperatures on metals than does oxygen, although the potential decline is much smaller. Still, I think that we must look for this mainly in the ready dissociation of the iodine molecule, always supposing that atoms react more rapidly than molecules, a supposition, moreover nearly a century old.

If this should be so, the action of a catalyst must be sought for in the increase of this dissociation.

Now, we know of a number of reactions where the catalyst forms undoubtedly a compound with one of the reacting molecules, which additive product then reacts with the second molecule to form the final product, with liberation of the catalyst, but even in such a case, which is called by many "pseudo-catalysis" (WAGNER, Z. Phys. Ch. 28 p. 48), I do not consider the *formation* of this compound as something essential without which the acceleration would not take place.

I certainly do not consider the formation of such an additive product as being without any significance, as it is an indication that the catalyst can exercise a particular influence on one of the molecules; the real increase of velocity is, in my opinion, due more to that influence than to the formation of the additive product, and in view of what precedes this, that influence consists presumably of an increase of the dissociation (and through this of the active mass).

It is, of course, obvious that a catalyst will act all the more energetically when the additive products are more labile. I have already mentioned platinum and now point also to the H-ions with which the formation of additive products, for instance when accelerating saponification, is far from probable. As a very lucid example, I mention the different catalytic influence which iodine and $AlCl_3$ exert on the transformation of yellow into red phosphorus.

From the researches of Brodie (Ann. de Ch. Ph. 1853 p. 592) which I have found fully confirmed, a small quantity of iodine can convert a large quantity of yellow phosphorus very rapidly into red phosphorus at 140°. (As in many other cases, there is a limit because the catalyst is precipitated by the colloidal phosphorus formed.

The velocity at the ordinary temperature is very small but becomes plainly perceptible at 80°. We are undoubtedly dealing here with a

case where the catalyst combines with the phosphorus to P_2I_4 ; this substance commences at 80° to dissociate measurably [so that its vapour density can only be determined at a low temperature (TROOST CR 95 293)] with separation of *red* phosphorus. We may, therefore give here a fairly positive answer to the question: How is it that the second division process proceeds more rapidly than the original ? Because P_2I_4 dissociates much more rapidly than P_4..

But this is after all but a lucky circumstance, the real cause must be. sought in the fact that in order to obtain P_2I_4 the P_4 molecule must be dissociated to begin with. With $AlCl_3$ I have not been able to find an additive product, only some indications that, besides the allotropic transformation, a trace of PCl_3 is formed (even with perfectly dry substances the manometer, after a few hours' heating to 100°, showed a slight increase of the vapour pressure).

The fact that the red phosphorus formed has in a high degree the property of coprecipitating the catalyst might perhaps indicate the possibility of a compound being formed between yellow phosphorus and $AlCl_3$; from the above it follows that there is a possibility of a certain reciprocal influence [1]) but I attribute this coprecipitation to the colloid properties of the red phosphorus, which, when obtained from solvents and also under the influence of rays of light, carries with it a certain quantity.

But even if an additive product is found, the existence of this substance is no more the cause of the acceleration than it is in the case of P_2I_4.

On the contrary, I consider the formation of a compound of the catalyst to be a case of "poisoning", caused by one of the reacting molecules, just as arsenic and prussic acid are poisons for platinum, because in combining with it, they prevent the entrance of O_2 and H_2 (respectively SO_2); just as ether is a poison for $AlCl_3$, because it unites with it to a firm compound, which does not decompose until over 100', the temperature at which the catalyst again recovers itself.

Now, I cannot deny that we have not advanced much further with this dissociation theory (which is also not absolutely novel) for the question is now: How is it that a catalyst accelerates the dissociation? But my object was to point out that the formation (and eventually the admitting of the formation) of intermediate products can certainly never lead to an explanation of the catalytic phenomena.

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[1]) I have also found a similar reciprocal influence in the action of C_2H_5 Br on $AlCl_3$ in which C_2H_5Cl and $AlBr_3$ are formed; it undoubtedly points to a dissociation.