REACTION LIMITS, REACTION REGIONS AND REACTION SPACES

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INTRODUCTION

Since Humphry Davy in **1815** determined the range of explosibility of mixtures of "firedamp" with air (l), many researches have been made on the *limits* of *inflammability* of mixtures of a combustible gas or vapor and air or oxygen. The extensive literature relating to this subject has been collected in several publications **(2).** For a survey of the principal experimental results and the theoretical views which bear upon the subject, we can, therefore, refer to those reviews.

Next to these investigations, which are also of great practical value, the *dust explosions* have given rise to much research work, also on account of their disastrous results **(3).** Only a few limits have been determined.

It is also well known that a reaction, started locally in a mixture of *solid substances,* may propagate itself through the whole mass, if the composition of the mixture is suitable. We have only to call to mind the old gun powder, made from charcoal, sulfur and saltpeter, and the different mixtures in fireworks, etc. As lecture experiments there may be cited the propagation of the reaction in mixtures of iron and sulfur, of magnesium and silica and the like. The importance of the study of such reactions has become obvious since Hans Goldschmidt **(4)** applied the alumino thermic reduction to his "thermites." When reading W. Prandtl's "Thermitreaktionen" *(5)* we get an impression of the great variety of reactions taking place in a similar way.

If we restrict ourselves in the first place to mixtures of two substances, we observe—just as with mixtures of a combustible gas or vapor and air or oxygen-that the reaction takes place only between two *limits,* which we have called *reaction limits.* Such limits were determined by us for instance in the case of iron, magnesium or aluminium and sulfur (6) *(7),* and potassium dichromate and sulfur or aluminium (8). In the case of ammonium dichromate and iron or sulfur (9) only one limit is observed, as the reaction started in pure ammonium dichromate will also propagate itself.

Although the study of the reactions between binary mixtures of solid substances presents many interesting points of view, such as the determination of velocities **(43),** we shall confine ourselves here chiefly to ternary and quaternary mixtures. From these we choose those containing only gases or vapors and those containing only solid substances.

I. TERNARY MIXTURES

A. First of all we shall consider reacting mixtures of three gases. If we regard air as one substance (viz. less reactive oxygen) our attention is drawn first to explosions of mixtures of *two combustible gases or vapors and air.* Such mixtures have been studied exhaustively since H. Le Chatelier published (10) his well known formula $\frac{n'}{N'} + \frac{n''}{N''} = 1$. In this formula n' and n'' are the volumes of the two combustible gases which, mixed together with the quantity of air needed to make the total volume 100, just produce an inflammable mixture. N' and N'' are the limits of inflammability of the two gases taken separately. Le Chatelier considered this relation almost as a matter of course. He applied it in the first place to determine the percentage of methane present in mine air. He added so much of a combustible gas, of which the lower limit of inflammability is known, that the lower limit of inflammability of the mixture was reached. As N' , n'' and N'' were known, he could calculate n'. \mathbf{N}'

P. Eitner (11) remarked that Le Chatelier's formula indicates that a combustible gas, mixed with other gases, produces the same volume of inflammable mixtures gas-air, as when alone. But, he adds, then the formula must also hold good for mixtures of more than two combustible gases. Thus the general form will be **(12):**

$$
\frac{n'}{N'}+\frac{n''}{N''}+\frac{n'''}{N'''}+\ldots=1
$$

Le Chatelier and 0. Boudouard (13) found the formula to apply to mixtures of CO and C_2H_2 . Slight deviations were observed with mixtures of CO and $H₂$.

Inflammable mixtures were found to be:

Eitner remarks that the relation will only hold if the gases do not hinder each other's inflammability. Therefore he does not expect that it will prove exact for the upper limit of inflammability, as in that case there is not a sufficient quantity of oxygen to burn both gases completely. In fact he calculates for the upper limit of inflammability of water gas (49.15 per cent CO, 49.85 per cent H₂, 1 per cent air): $\frac{n'}{N'} + \frac{n''}{N''} = 0.949$.

Among those who have tested Le Chatelier's formula should be mentioned especially H. F. Coward, Ch. W. Carpenter and W. Payman (14) and A. G. White (partly with T. W. Price) (15).

It was especially White who, in the course of his extensive researches, has found many deviations from this formula.

Graphical representation

If we consider the quantities of the two combustible gases as coordinates (16) we are able to represent the limiting mixtures by points in a plane. If the mixtures obey the formula of Le Chatelier we get a straight line. For if we consider n' and n" as variables, *the formula is the equation of a straight line,* N' and N ", the lower or upper limits of inflammability, being the intercepts on the axes. An example of nearly straight lines for the lower and upper limits is afforded by the experiments of Coward,

Carpenter and Payman (14) with mixtures of CO and H₂ (fig. 1). The region between those lines and the two axes we have called

explosion region. All the mixtures represented by points outside this region are non-inflammable.

More perceptible deviations from straight lines are found if we represent graphically White's results (17) with mixtures of *CHI* and H_2 (fig. 2) or with mixtures of NH_3 and H_2 (fig. 3). But in the latter case ammonia shows limits of inflammability only with upward propagation. For if we represent graphically his results

FIG. 4. EXPLOSION REGION NH₃-H₂-AIR DOWNWARD PROPAGATION

FIG. 5. EXPLOSION REGION NH₃-H₂-AIR

with downward propagation we get the curve shown in figure **4.** As we see, the explosion region does not reach the vertical axis, which means that in the case of downward propagation (under the circumstances of White's experiments), no mixture of **NE13** and air alone will explode.

These graphical representations show the deviations from Le

Chatelier's formula much better than tables of figures; even when these tables give the deviations in per cents.

FIG. 7. EXPLOSION REGION $NH_3-N_2-O_2$

But they also show clearly the influence of different circumstances, such as: downward propagation and upward propagation.

How much the extent of an explosion region may be changed

when replacing air by oxygen is shown by the following diagrams figure *5* and figure 6 (18). Here we have represented the results in equilateral triangles.

We shall now consider mixtures of *one combustible gas (or vapor), one non combustible gas (or vapor) and air (or oxygen).*

Let the non combustible substance be nitrogen and the combustible one ammonia. How the limits of inflammability of

FIG. 8. THE EXPLOSION REGIONS $CO-CHCl_3-AIR$, $CO-CH_2Cl_2-AIR$ AND $CO-CH_3Cl-_{AIR}$

FIG. 9. THREE TYPES OF EXPLOSION REGIONS OF FREQUENT OCCURRENCE IN PRACTICE

ammonia-oxygen-mixtures change when gradually replacing the oxygen by nitrogen is shown in figure *7.* The limits approach each other and coincide at about **32** per cent of oxygen (19).

In the same way the vapor of carbon tetrachloride makes the limits of inflammability of methane in air coincide when the vapor content reaches a certain figure.

In our experiments (20), with a tube of about 1.5 em. internal diameter, a small spark and downward propagation, a vapor content of 7.8 per cent was sufficient to make the mixture of methane and air non inflammable; in those of H. F. Coward and G. W. Jones (21) with a tube of about *5* cm. internal diameter, a flame of a spirit lamp as igniter and upward propagation a vapor content of about 12 per cent CC1, was necessary. The difference between these figures illustrates the influence of different experimental conditions on the extent of the explosion region **(22).** Carbon tetrachloride also narrows the limits of inflammability of hydrogen-air-mixtures **(23)** and acetylene-air-mixtures **(23)** and

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FIG. 11. TWO OF THE THREE GASES FIG. 12. ONE OF THE THREE GASES

has a strong extinguishing influence on the inflammability of carbon monoxide-air-mixtures **(24).** The explosion region CO-air-CC1, is therefore very small.

That of carbon monoxide, air and chloroform vapor **(24)** is also a small one (fig, 8). That of carbon monoxide-air-methylene chloride is larger and already approaches somewhat the left side of the triangle. The explosion region carbon monoxide-airmethyl chloride reaches the left side of the triangle; the lower limit of inflammability of CHsC1-air mixtures is indicated in figure 8 by C, the upper limit by D. Figure 8 thus shows clearly that the incombustibility of CCI, decreases when chlorine is replaced by hydrogen.

The explosion region $CO\text{-}air\text{-}CH_2Cl_2$ appears to be intermediate between that of CO -air-CHCl₃ and that of CO -air-CH₃Cl. When a vapor shows an explosion region with CO or another combustible gas resembling that of $CO\text{-}air\text{-}CH_2Cl_2$, we have to do with a substance which, although not combustible, tends to become so. It may become combustible at a somewhat higher temperature.

FIG. 13. EXPLOSION REGION N_2O -ETHER- O_2 (AIR)

In what measure the region approaches the left side of the triangle will depend on the combustibility of the gas with which we mix the methylene chloride vapor **(25).**

The three types of explosion regions drawn in figure 8 and also, in outline, in figure 9 are to be found in the case where the three gases A, B and C can react with each other and also C with A and C with B, but not A with B. This case, therefore, is not the simplest one. But it has been treated here in the first place, because in practice it occurs frequently.

From a systematic point of view it would have been better to begin with mixtures of *three gases which can react upon each other* *and also two* by *two.* Such a case is represented in outline by figure 10; it has not been investigated experimentally.

As an example may be cited the system hydrogen-oxygensulfur vapor (26).

If the *three gases* are *endothermic* and the impulse (for instance a spark) is strong enough to start in each of them a reaction which propagates itself (without one or two of the others being present). then the explosion region will fill the whole triangle; if two of the

FIG. 14

three *gases* are *endothermic* or only *one* of them, we can expect explosion regions represented in outline in figures 11 and 12 **(26).**

Interesting explosion regions will be found, using, for instance, mixtures of acetylene, carbon disulfide vapor, nitrogen oxide or nitrous oxide with other gases.

A few cases have been studied already. We mention in the first place the systems: ether vapor-oxygen (or air)-nitrous oxide and chloroform vapor-oxygen-nitrous oxide (27). But in these cases only a small spark was used, which did not start a reaction in nitrous oxide alone.

The explosion regions $(C_2H_5)_2O-O_2-N_2O$ and $(C_2H_5)_2O\text{-}air-N_2O$ are represented in figure **13,** viz., ADCB and ADCE. When the spark is strong enough to start in nitrous oxide (without ether vapor) a reaction which propagates itself, the line AD will revolve round **A,** and cut the left side of the triangle.

The system chloroform-oxygen-nitrous oxide investigated in the same way (as the other two mentioned above) appeared to have no explosion region.

FIG. 15. REACTION REGION $Al-SiO₂-S$

Some experiments with carbon disulfide have been made by A. G. White **(28)** who determined the lower limits for the propagation of flame downward in mixtures of acetone, benzene and acetaldehyde with carbon disulfide and air. These limits are represented by me **(29)** in figure **14.** The curves show an interesting flexion.

Of practical value will be, for instance, investigations of the systems: acetylene-acetone vapor-air and such like, with a view to the question of not dangerous, dissolved acetylene; acetylenesaturated hydrocarbons (for the manufacture of carbon black) ; nitrogen oxide-carbon disulfide-nitrogen (or carbon dioxide) to supply a source of a constant actinic light, etc. The determination of the velocity of reaction in different parts of the reaction region will in several cases give an indication as to the mixtures to be used for special purposes.

B. We will now turn our attention to *mixtures* of *three solid substances.* Here we have been able to realize **(30)** the reaction region in its simplest form (a closed reaction region), using

FIG. 16. REACTION REGION Fe-S-SiO₂

FIG. **17.** REACTION REGION Fe-S-AI

mixtures of dried silica powder, flowers of sulfur and fine aluminium powder. A mixture of iron and sulfur $(1 \text{ Fe} : 1 \text{ S})$ served as a fuse, which was, in its turn, ignited by means of a small gas flame. The reaction region is depicted in figure 15. Its extent depends on the conditions of the experiment. So an extension towards the A1-S axis is therefore to be expected with the use of a more powerful igniter .

That the region is of a greater extent under the conditions given

by Kuhne (31) and Holleman (32) follows from the fact that the mixture 200 g. Al, 250 g. S and 180 g. $SiO₂$ falls outside the region determined above.

It is our intention to measure the reaction velocity in different parts of the region.

The region B_2O_3 -Al-S and similar ones will also be investigated. The three types of reaction regions, which we have observed, using mixtures of carbon monoxide and air with the vapor of

FIG. **18. REACTION** REGION Fe-S-Mg

chloroform, methylene chloride or methylchloride (figs. 9 and 10), have been realized also with the following systems (33): Fe-S- $\rm SiO_2$ (figure 16), Fe-S-Al (figure 17) and Fe-S-Mg (fig. 18). The substances were used in the form of powders; the mixtures were fired by means of a mixture of iron and sulfur $(1Fe:1S)$ to which a small flame was applied.

The influence of the size of the particles of the reacting substances and of the nature of the igniter has been studied with the system Fe-S-A1 (34). Thus we see the possibility of a closed reaction region extending itself to one or more of the sides of the

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triangle. Extension to one side may give as results figures 16 and 17. Cases of extension to two sides of the triangle are drawn in figure 18 and figure 19 (8). Extension to all three sides (fig. 20) has been observed with potassium dichromate, sulfur and aluminium which react upon each other and also two by two (8).

Interesting reaction regions will be found, when using *endothermic* solid substances (compare p. 26). If one of the substances is endothermic and the impulse is strong enough to start a reaction which propagates itself also in the pure endothermic

substance, then the reaction region will extend to the corner of the triangle representing that substance.

This may also be observed when an exothermic substance decomposes (but not into the elements) with evolution of so much heat that the reaction, started in one part of the substance, propagates itself through the whole mass. **A** well-known example is ammonium dichromate. Mixtures of this substance with potassium chloride and potassium sulfate produce a reaction region drawn in figure 21 (9). If we make mixtures of ammonium dichromate with two substances which react upon each other, for instance iron and sulfur, the reaction region must become much larger. For it must then reach the opposite side of the triangle. The reaction region is depicted in figure **22** (9). A narrowing occurs at HK. This narrowing gave rise to an investigation communicated on page **41.**

FIG. 20. REACTION REGION $K_2Cr_2O_7-Al-S$

FIG. 21. REACTION REGION $(NH_4)_2Cr_2O_7-KCl-K_2SO_4$

The limiting curve DEKC also shows a bulge at E. Now bulges had already been observed with reacting gas mixtures (see for instance figure **14).** We hope to be able to account for the bulge at E by a quantitative investigation of the reactions taking

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place in the neighborhood of the bulge and in other parts of the reaction region.

The determination of reaction regions of mixtures in use as explosives, will evidently give results which may be useful in practice. For this purpose we started an investigation with mixtures containing gun cotton. In the first place we chose such mixtures as can be gelatinized. Reaction regions were determined and reaction velocities were measured. The results will be published before long **(44).**

FIG. 22. REACTION REGION $(NH_4)_2Cr_2O_7-Fe-S$

11. QUATERNARY MIXTURES

A. Just as with the ternary mixtures we shall first treat the *reaction space* of *mixtures of four gases or vapors.*

If we mix three combustible gases with oxygen or air (regarding air as one gas (a less reactive oxygen) we may have to do with mixtures which follow Le Chatelier's formula **(14)**).

In that case the points indicating the limit mixtures will be an as one gas (a less reactive oxygen) we may have to do with
mixtures which follow Le Chatelier's formula (14)).
In that case the points indicating the limit mixtures will be
found in a plane, for the formula $\frac{n'}{\overline{N'}}$ equation of a plane, if we consider n', n" and n"' as variables, N' , N'' and N''' being the intercepts of the plane on the three $\mathbf{n'}$ $\mathbf{n''}$ $\mathbf{n'''}$

axes. If the formula holds good not only for the lower but also for the upper limits, we shall get an explosion space enclosed by five planes, *viz.*: the three coordinate planes and the two planes

FIG. 23. EXPLOSION SPACE $NH_3-C_2H_5Br-O_2-N_2$

represented by Le Chatelier's formula **(35).** In general, however, we may expect an explosion space enclosed by a partly curved surface.

The case of two combustible gases or vapors, one noncombustible gas and oxygen has been studied by taking ethyl bromide vapor, ammonia, nitrogen and oxygen (19).

The explosion space is represented by figure **23.** Its base is formed by a triangle of which the corners represent $NH₃$, $C₂H₅Br$ and O_2 . S and T represent the limits of inflammability of $NH₃$ with oxygen, R indicates the lower limit of inflammability of $C₂H₅Br$, the upper limit W cannot be determined, as the oxygen is saturated with ethyl bromide vapor at Q.

If we now draw a triangular prism, the base of which is formed

FIG. 24. EXPLOSION SPACE C₂H₃Br-NH₃-O₂-N₂: HORIZONTAL SECTIONS AT DIFFERENT PERCENTAGES OF OXYGEN

by the triangle, we can measure the nitrogen upwards along the parallel edges of the prism, which are at right angles to the plane of the base.

Making horizontal sections at different percentages of oxygen. we get different explosion regions of which four have been drawn in figure **24.**

If the O_2 -N₂-mixture contains 95 per cent of oxygen the explosion region is RSTVQ. The line of the upper explosion limits TV ends in V, because the gas mixture is then saturated with ethyl bromide vapor. Also when the O_2-N_2 -mixture contains **62.5** per cent of oxygen the line of the upper limits (beginning in P) does not reach the horizontal side of the triangle. If **43** per cent of oxygen is present in the O_2-N_2 -mixture the explosion region is limited by the curves HG and JF and two sides of the triangle. With 28 per cent of oxygen in the O_2 -N₂-mixture the explosion region is much smaller; it is limited by the curve BDC and only one of the sides of the triangle. Mixtures of NH_s and an atmosphere containing **28** per cent of oxygen are not inflammable. The explosion space, drawn in figure **23,** contains a metastable part UVLKQW. There only supersaturated vapor could have been used. The experiments show that there is a regular decline from the top of the curve which limits the explosion region $C_2H_5Br-O_2-N_2$ to that which limits the explosion region $NH₃-O₂-N₂$.

It would be interesting to find a space figure in which a horizontal section shows an explosion region which does not reach a side of the triangle. That is to say the case that the explosion region BDC of figure **24** has contracted to a region surrounded by a closed curve **(36).**

Another case of four gases or vapors will be treated here, viz., methane-air-carbon dioxide-carbon tetrachloride vapor **(37).** This system has been investigated (as part of a systematic research on the prevention of mine explosions), in order to test the possibility that two inhibitors will produce an enhanced effect, when working together, so that prevention will be attained with a smaller percentage of the two together than with either separately.

The damping possibilities of carbon dioxide on methane-air explosions had already been investigated by H. F. Coward and Hartwell **(38).** They found that the explosion limits coincided with 25 per cent $CO₂$. Previous to this, experiments had been carried out in this direction by P. Eitner **(ll),** J. K. Clement **(39)** and G. A. Burrell and G. G. Oberfell (40) by partially replacing the oxygen of the air with $CO₂$. Clement (39) also determined the damping action of carbon dioxide in mixtures of air and natural gas $(83.1 \text{ per cent } CH_4, 16.0 \text{ per cent } C_2H_6, 0.9 \text{ per cent }$ N_2). He found in a Hempel burette, that the explosion limits coincided with 20.5 per cent COz.

The influence of carbon tetrachloride on the explosion limits of methane in air has been studied by ourselves (41) and, under different conditions, by H. F. Coward and G. W. Jones **(21).**

FIG. 25. VERTICAL SECTION OF THE EXPLOSION SPACE $CH_4 - AIR-CCI_4-CO_2$

If it had been our purpose to make a complete study of the quaternary explosion region methane-air-carbon dioxide-carbon tetrachloride vapor, we might after determining the ternary region methane-air-carbon tetrachloride vapor, have investigated the alteration of the latter produced by the addition of carbon dioxide. The carbon dioxide contents could then have been measured on an axis perpendicular to a triangle representing the ternary region.

For the sake of simplicity, however, we investigated only a vertical section through the explosion body, that is, we considered a plane, perpendicular to the triangle and passing through the CCI, corner and through the point on the opposite side of the triangle representing 9 per cent methane (this being one of the most highly explosive of such mixtures).

The section of the explosion body in this plane thus appears as a curve between rectangular coordinates, the horizontal axis being the CCl₄ axis and the vertical the $CO₂$ axis, the origin

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representing the methane-air mixture. In order to make this mixture non-explosive 9 per cent $CO₂$ or 6.4 per cent $CCl₄$ was necessary (in our explosion buret). The section is shown in figure *25.* As may be seen from this graph, the two inhibitors have a fairly strong influence on one another. The figure shows that, for instance, 1.8 per cent CCL_4 and 2.7 per cent CO_2 , or 4.5 per cent of a mixture of $CO₂$ and $CCl₄$ vapor containing 40 per cent of the latter substance, is necessary to make the methaneair mixture non-explosive. In a mine more than **4.5** per cent would be necessary, as the explosion region would be greater (less loss of heat to the surroundings, the possibility of upwards propagation, of more intense ignition, etc.). As 40 per cent CCl_4 is a greater content than corresponds to carbon dioxide saturated with CCI4 vapor, the mixture would have to be added

FIG. 28. REACTION REGION Mg-Al-S

in the form of a CC1, spray by means of a cylinder of liquid carbon dioxide.

Let E represent in figure **26** the explosion region of methane with air and a certain mixture of $CO₂$ and $CCl₄$. Now if such a mixture is introduced into a pocket of mine gas and if the composition of the CH_{4} -CO₂-CCl₄ mixture obtained be represented by S, then, if the line S-air lies outside the explosion region, an explosive mixture will never be obtained on ventilating with air. An explosive mixture would, however, be obtained if the composition were represented by s'.

In practice the amount of $CO₂$ and $CCl₄$ required will not be known. However, in general the spraying of CCl_4 with liquid $CO₂$ might be of service as a fire extinguisher and, in some cases, could be applied to prevent the occurrence of explosions.

It still remains desirable to find a *harmless* substance, or mixture of such substances, which used *in small quantities* will exert a complete retarding action on methane explosions. systematic research in this direction is being made in our laboratory.

B. Till now only two *reaction spaces* have been investigated using four solid substances.

In the first place a simple system was chosen, *Wix.,* Fe-Mg-A1-S **(42).** The reaction region Fe-M-S and Mg-AI-S are drawn in figures **27** and 28.

Let us now look at figure 29. In the triangle Mg-Fe-S we see the reaction region JKLH of those elements, J and H being the reaction limits of Mg with S, K and L the reaction limits of Fe with S. We now add Al and measure its quantity upwards along parallel lines, which are at right angles to the plane of the triangle. The reaction limits Mg-S and Fe-S will approach each other and coincide at certain percentages of AI. The horizontal projections of the tops of the two curves lie at G and F respectively. The upper part of the figure must be imagined to be folded at the line $Mg-Fe$ and used as a vertical projection. Thus the vertical projections of the two tops mentioned above lie at X and E respectively.

If we now use mixtures of Mg and Fe (containing *75* per cent Mg, 50 per cent Mg or **30** per cent Mg) instead of Mg or Fe alone, we get curves whose tops have B, C and D as vertical projections. The horizontal projections are to be found on the dotted line between G and Fe.

FIG. 39. **HORIZONTAL AND VERTICAL PROJECTION OF THE REACTION SPACE** Mg- Fe- S- **AI**

The line which passes through the five tops shows a regular slope (see the vertical projection ABCDE).

Although we have not constructed the whole reaction space, figure **29** gives a fairly good idea of its form.

In the event of all three metals showing reaction limits with

sulfur, representation in a regular tetrahedron would be preferable. This case would have occurred if the circumstances of the experiment had been of such a nature that the aluminium and sulfur had shown reaction limits.

The second system studied (ammonium dichromate-sulfuriron-silica) was a continuation of that described on page **31.** In the region represented in figure **22** a narrowing at HK occurs. This opened the possibility that on the addition of a deadening substance, such as silica, the region would split into two regions.

FIG. 30. HORIZONTAL SECTION THROUGH THE REACTION SPACE $(NH_4)_2$ Cr_2O_7 -Fe-S-SiOz **(12 PER CENT SILICA)**

Therefore a horizontal section was investigated through the quaternary space, which is obtained when the quantities of silica are set out vertically, starting from the plane of the region $(NH_4)_2Cr_2O_7-S-Fe$. As about 9.5 per cent silica appeared to make H and K coincide, a section was taken at **12** per cent silica in order to be sufficiently above the place of coincidence. The resuIts of the experiments (8) are represented in figure **30.** The two regions into which that in figure **22** has divided already lie fairly far apart. The projection E is still present in the left hand region.

This short review of what has been investigated in the domain of reaction limits, reaction regions and reaction spaces shows what has been achieved so far and part of what remains to be done. In every direction there is a fair chance of discovering interesting facts.

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