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Archiv.

Sv. 3372.

91.

V Brně, 10. ledna 1931.

Ant. Šimek
Popraven 1942

Ládvutný pane profesore,

Krátko se právě z několika-
desítky pobytů ve Vídni,
vzpomínám na Vašem jubileu
a přičinám, abyste Vám
vyslovil i své nejvůlejší
blahopřání, nežli jinými
slovy, abyste se vedle
zajisté početného uspo-
řádání našeho výsledky své
v našem vědeckém světě
jediněmu práce dočkal

V Brně, 10. ledna 1921.

Ant. Šimůnek
Převrácen 1942

Ládvutný pane profesore,

Krátko se právě z několika-
desítky pokytnu ve Vídni,
dovídám se o vašem jubileu
a spěchám, abych Vám
vyslovil i svou nejvělejší
blahopřání, nežli nyní
klavíř, abyste se veďte
zajisté pracovatého uspo-
řádku nad výsledky své
v našem vědeckém světě
jedině práce počal

ve zřeteli generace našeho
národa, jež by svou
objektivní zhodnotila oceňující
hodnotu vašeho výkonu
myšlenkového i technického,
učinila základem svého
nážeru přírodovědeckého
jméno slavovisko než je
zaujímá Vy.

Vám, slovníkům pane profesore,
v hluboké úctě oddaný

—
Rudolf Müller

Práce inž. F. Waldovi
v přátelské snaze
přeložit.

Collection III., No 1—2, 1931

des travaux chimiques de
Tchécoslovaquie.

of Czechoslovak Chemical
Communications.

FOUNDATIONS OF A THEORY OF CHEMICAL OPERATIONS

by F. WALD.*)

1. The theory of chemical operations is based on old experiences known to all chemists and besides this also on self-evident propositions adduced from this experience. These abstractions did not originate only in my mind, for they are a common property of natural science, but the *logical construction* of the theory following from them is my own work.

Here and there I was obliged, in the interest of a clear exposition, to use familiar terminology in an altered sense which, of course, I shall explain precisely; where I feared, however, that the altered sense of a word would be too easily mistaken for the usual one, I did not hesitate to use a term more adequate to my purpose.

Hitherto chemistry has been delivered to us as a science, in which the chemist entirely disappears as a wholly superfluous factor beside nature, so that his activities are mentioned only in his biography or obituary, though chemistry is an experimental science on which an extended technology is founded. It is true, there are going on in nature chemical processes without any cooperation of man, which often even baffle any influence of his merely owing to their grand scale, but here nevertheless at least an *accidental* contact of different substances under more or less *haphazard* external conditions determines the nature of chemical phenomena.

I could have called this essay of mine either a theory of chances or a theory of operations, but I have preferred, of course, a title appropriate to a laboratory or a factory, which both are managed by *man*, who reflects upon the chemical phenomena observed both in dead as well as in living nature according to his experiences made in the sphere of his activity. Man *shares* with nature the control of chemical phenomena. In a laboratory or in a factory nothing happens

*) Published first in Czech in the Sborník Přírodovědecký, edited by the
»Česká akademie věd a umění« (Czech Academy of Science and Arts), 1929, No. VI.

Přeložil Prof. Dr. Simek.

against the will of the chemist as long as he either looks after the things, or is not led into an error by some chance, nor overcome by an accident.

Nature is thus not an absolute ruler in chemistry sharing its command with man; each of both factors has its own domain of influence which may be characterized by the contrast: *natural law* — *human will*.

This free will, however, does not act telepathically, but by means of appropriately intended *actions*.

I should act unfairly, if I were to conceal, that the whole manner of thinking which I disclose in this communication was really conveyed to me by the physiologist Professor F. Mareš in our discussions some 25—30 years ago.

Only the more detailed elaboration of this mode of thinking from the chemist's view-point is my own intellectual property.

2. In sharing the rule between man and nature it naturally happens, that man is originally desirous of such chemical phenomena which nature does not permit, at least so far as the man does not perhaps find new means. Thus all efforts of alchemy to produce gold from base metals failed and it seems that they will remain useless for long yet. However, great benefit arose from such endeavours, for man could thus find out that such changes are quite *impossible to attain* in chemistry, even through efforts however long lasting.

The chemists have succeeded to condense the experience, that countless phenomena are impossible, into a *positive* statement that *mutually unchangeable elements continue to exist concealed in the substances.**)

I do not intend now to consider the question, whether this way of expressing the established *facts* is the only possible one, or whether it would be possible to substitute a more suitable one for it; we are here satisfied with the knowledge that the *facts*, on which the idea of perpetuity of the elements is based, are absolutely *trustworthy*. The whole chemical literature is founded on it, and when nevertheless a more suitable way would be found, it could yet be maintained for a long time *beside* the familiar view, e. g. in solving special problems, otherwise the treasures of the older chemical literature would become, at least for a certain time, incomprehensible. Only some of the *con-*

*) It is not necessary in this connection to regard the more recent observations on radioactive elements, because thus only the *number* of the immutable elements would be changed, but the magnitude of this number is wholly irrelevant as long as it is not reduced to one.

clusions from these facts, which have till now been overlooked, will be treated in this paper.

Chemistry has ascertained (against the views current in the first two decades of the nineteenth century) that there exist whole series of different chemical compounds having absolutely identical percentage composition (proportion of elements composing them); we call them *isomeric* substances (in the broadest sense of the term) distinguishing different kinds of isomerism, which does not, however, matter at all for us here. It suffices however, that there exist many different compounds of the general formula $C_n H_{2n}$, where n may be an integer from two onwards. Let the number of these compounds having the same n , be *fifty* (considering the possibility of the same »constitution«), where this number is again quite indifferent; it would suffice, that it is only larger than two or three.

Chemical processes, in which one element would change into another, are wholly impossible; there are however, certainly possible, at least *sometimes*, such reactions or series of reactions, which lead to a change of a compound into another of the same composition; otherwise different elements would be involved. When we have, on the whole, fifty such substances of the same percentage composition, there will be altogether

$$\binom{50}{2} = \frac{50 \times 49}{2} = 1225$$

changes *possible*.

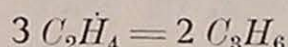
Nobody would admit the idea, that it could depend upon the *will* of any of those *compounds*, into which compound it desires to change, because then each of them would have a choice among fifty different possibilities, namely whether it wishes to remain as it is, or to change into one of the other forty nine compounds. The given compound will thus remain so *long unchanged*, till we ourselves make its change possible. The *chemist* himself must have the possibility of choosing among at least forty nine suitable ways, in order to determine by means of them, which new compound of the same percentage composition should be formed out of the compound originally present. Besides this he does not take thereby into consideration the actual direction of the reaction; really, it is indifferent to him, whether he changes the compound a into b , or whether perhaps on the contrary a will be formed from the given b .

3. It is necessary also to pay attention to further circumstances; chemistry, ascertaining that it never can, by the means known hitherto, change e. g. carbon, C , into hydrogen, H , (and that just for

this reason they are different elements), does not have in mind a *simple* process describable by an equation like $xC = yH$, but it wants to say, that even the *most complicated series or net-work* of chemical changes hitherto known does not give such a result.

Thus, if we desire to change a definite member of the series $C_n H_{2n}$ into another one, we must not at the same time expect, that this process should be *simple* and confined only to the one olefine $C_n H_{2n}$ as the original substance and another olefine as the only product, though it would be irrelevant for us, which of both is the initial and which the resulting substance. The desired change is allowed to be a final (*algebraic*) result of a whole *series or net-work* of reactions; it is thus permitted to use any auxiliary substances in any number of simple reactions. A continuous series or net-work of reactions arises in such a way, that one uses in each following reaction at least one product of some foregoing reaction. We are here directly compelled to *use up* a part of the intermediate products, though not completely. It is, however, possible to use up completely at least some of them, and then the final result of all reactions of the reaction series or reaction net-work can be expressed by a *single comprehensive equation* containing less substances than we have actually used or gained.

4. In order to admit in chemistry, that an isomeric change has been accomplished, it suffices, if at least two comprehensive equations of reaction series or reaction net-works are found, which added *algebraically* give as the final result e. g.



(or inversely), because all auxiliary substances and their products disappear from the calculation, only the two olefines remaining.

I am not to blame, if this my exposition will seem to somebody too intricate; the *thing* itself does not permit a simpler explanation, if it should be elucidated properly also for a whole series or net-works of reactions. The mere *composition* of both substances can be determined, of course, very simply by burning both substances and ascertaining, that — the consumption of oxygen being the same — identical products are obtained in both instances, namely the same amounts of water and carbon dioxide.

Only now we have defined properly the accurate meaning of the word *impossible* in the statement, that a transmutation of elements is impossible, and therefore a mutual transformation of compounds of the same composition *possible*. Isomeric substances (in the widest

sense of this term) were only a suitable instance for this explanation. The words possible or impossible are not, of course, without any definite meaning, but have *in addition* to this here also a *very uncertain* meaning.

5. On another occasion I intend to treat more fully those instances, where changes hitherto *impossible* in chemistry are involved. Now I am pursuing another series of thoughts, desiring to know where chemical changes are *possible*, which by no means yet does signify *actual* (real) changes. These have obviously under given circumstances a very definite *direction*, and in *time* their beginning and end.

The cooperation of the chemist in the control of chemical phenomena has the effect, that we can always confine ourselves to a *single* (isolated) reaction, because the net-works and series of such reactions can be always disentangled into their simplest parts.

Man can influence the substances in two ways only: either by means of other *substances*, or by means of suitable forms of external *energy*.

6. The hitherto prevailing chemistry instructs us with an absolute confidence, which changes of substances are *impossible* with the aid of means known to us up to now, but it leaves us in doubt, under which conditions the individual *possible* changes become *real*; surely, chemistry has accumulated also in this direction many valuable experiences, but whilst the elements are scrupulously recognized and counted, we have no systematically ordered knowledge about the number and nature of means, by which the *possible* changes of substances are accomplished.

Even for the reason, that chemistry, pure and applied, is based throughout on *experimental* knowledge, all means, by which the possible chemical changes of substances are performed, have in one sense the same character: they are throughout *performances depending on the free will of the experimenter*. Surely, considering the still incomplete investigation of certain phenomena, changes also exist, which are not controlled entirely by us; then the whole effort of the chemist is to remove this unsatisfactory state and to recognize the conditions of the phenomena in question so completely, that he could control them and be able either to realize or to prevent the changes by his will. In the well explored fields of chemistry we may call every act of the chemist, which is directed to a realization of possible chemical changes, a chemical *operation*. From this definition then exclude themselves some phenomena (like certain changes of radio-

active substances), as far as the chemist cannot influence them at all because then there is in our sense no difference between possible and real phenomena, and only actual processes are going on.

7. The most fundamental part of this investigation is, in my opinion, a clear statement of a very old experience known to every chemist, but never formulated before, that very often a *single* operation does not suffice to accomplish a "*possible*" chemical change, and that for this purpose, there is necessary *more than one* operation generally, of course, a *small number* of them, if we confine ourselves to *individual* reactions.

"Possible" changes, which are *not* realized because *all* conditions, are not fulfilled, could be called with the same right *impossible*; but then confusions would arise, because we have distinguished already in *another* sense between possible and impossible changes, and it is necessary to use words always in the same sense; for this reason it is not admissible to use these terms otherwise than they were used previously.

Before the discovery of isomerism in about 1820, chemistry knew only *two* different states of the same matter, namely the state of "physical mixtures" and that of "chemical compounds".

The old discrimination of the physical and chemical states was retained, it is true, till now, but there are not always only *two* such states of "the same" substance, but a whole series of them is possible. Formerly it was possible to consider all external influences conditioning the one or the other state as fully equivalent and their dissimilarity as indifferent. From that time, however, it would have been advisable to pay attention to their *diversity*.

8. The chemist controls by his operations the phenomena studied by him not only so far that he realizes them after his will — as far as they are possible in the present time —, but that he knows to *prevent* them also; for this purpose it suffices, of course, to *omit any* of the operations necessary for the realization of the possible phenomenon.

Where more such operations are needed, it suffices, of course, to omit even one single operation, but it is admissible also to omit two or three or all operations respectively. When three operations are necessary to accomplish one reaction, the number of ways possible of preventing this reaction is given by

$$\binom{3}{0} + \binom{3}{1} + \binom{3}{2} + \binom{3}{3} - 1 = 2^3 - 1$$

The most usual way of such operations is so familiar to us, that we do not even speak at all about it; it is bringing into *contact* different substances.

The contact of a given substance with any other cannot be prevented on earth, but it is nevertheless possible to restrict it to the contact with substances which are quite indifferent, physically as well as chemically, to the given substance; the possibility of a satisfactory choice of different pairs of phases, of which at least one has a sufficiently stable form (being a solid), is thus the most common supposition for chemist's control over the possible changes of substances.

By means of indifferent substances the chemist can also determine the amounts of active substances, which he desires to subject to a chemical change, of course, only in so far as the individual quantities have at least microscopical dimensions.

9. From the foregoing it is evident, that a *mere* contact of substances cannot be under all circumstances a sufficient cause for bringing about an actual chemical change; very often, it is true, the direct contact of two substances is a necessary condition for the change to be *possible* at all, but the sole contact is not yet sufficient for the change to become *real*. Besides the immediate contact of at least two substances capable of a chemical reaction (if a single substance does not suffice) there are usually necessary for a chemical reaction further additional interventions (or operations).

Indeed, even physico-chemical phenomena (like a formation of a new phase) are not usually caused by a *mere* contact of the initial substances, requiring the simultaneous presence of nuclei of the new phase, e. g. minute bubbles or tiny crystals.

In order to avoid confusions we must remember, that the physical state of every body changes with pressure p , and temperature t ; speaking of a matter at rest we must really think of a continuous *surface* variety of the states at rest. Here we have in mind such instances, where the given matter "can" pass into at least two different surface *varieties* of states. The number of the *remaining* operations besides p and t must be *equal to the number of these varieties, into which the given system is still capable of entering, whereby it is assumed, that the present state of the system is a state of chemical rest.*

The word "still" is here used on purpose, because the present state of the substance (or substances) must be also possible.

10. We can think here of material systems in general, not only of the simple reactions, for even whole systems of substances cannot have any will. Where there is possible a *continuous* series of different states of rest, there must be at the disposal of the experimenter also an operation capable of a *continuous* gradation (e. g. measuring off of the amounts of mass and energy); where, however, only a final number of *discreet* states of *chemical* rest is involved, the experimenter must be able to dispose of as many *discreet* ways of operation, as there are possible *transitions* from the given state of masses in *chemical* rest into other states of chemical rest. In pure physics such instances as a rule do not occur.

The transition from one state to another must certainly take place through a *continuous* series of states, though not those of equilibrium, but the *persistency* of matter in a state of *chemical rest* is a proof, that the existence of those continuous transitions is not yet sufficient to make a transition into another state possible. This happens, when there are (under the same physical conditions) *more* states of chemical rest possible *than one*, and the dead matter should itself decide, which "way" it will go. For a possible transition conditions of a quite *different* kind must be lacking, and such can be always understood as *discreet* in contradistinction to the *continuously* variable physical quantities, which determine externally the present state of rest.

11. Such *discreet* operations are needed apparently only where — speaking metaphorically — the matter under given circumstances gets at a *cross-road*, and there must be at least as many such operations as there are different chemical ways leading from the crossing. I say *at least*, because it seems, that sometimes it is possible to induce the matter by various interventions to go the same way. Then, of course, we shall consider the interventions as equivalent and take always only *one* of them into our account.

With this restriction it is then evidently possible to make the statement, that for *matter at a chemical cross-road* the chemist must be able to apply as many *discreet* interventions, as there are different possible ways supplied by nature for changing the matter.

12. In order to have a concise term for the discreet interventions, I am choosing a technical term from physiology, namely *stimulus*.

Those interventions of the chemist, whereby variable *quantities* defining the present state of a given matter are changed *continuously*. I called already many years ago *actions*, and I still retain this term,

Where there is no *cross-road*, there only *actions* are involved, and these are capable of a continuous variation (like changes of temperature, pressure and of the quantity of matter). If several substances are involved in the reaction, the chemist instantaneously adds in his mind also the bringing of the substances into immediate contact; this, however, does not harmonize with the views here pleaded for, as the chemist always *can, if he pleases*, either bring into contact the chosen quanta of selected substances or not, whereby, of course, the indifferent substances are not considered.

We have an old term for a pair of substances, which do not react even when brought into contact, though we should expect, that they are capable of reaction and would certainly react under changed conditions. We call them *passive* substances in contradistinction to the *active* ones, which (under given physical circumstances) begin to react promptly, if brought into contact, and to *indifferent* substances, which do not react with one another at all. Of course, the discrimination between passive and indifferent substances has not been observed strictly, because it did not matter as yet. However, the origin of passivity is now quite clear: there has not been fulfilled some *discreet* condition of the expected phenomenon. Thus there happens either nothing at all, or something quite different than has been expected.*)

*) The last words contradict to a certain degree the foregoing considerations, but I doubt that one would be therefore inclined to attribute a free will to substances. There are still several difficulties about the phenomena of passivity and it seemed sometimes, that the activity of (metallic) chromium can change periodically into passivity and, what is more, that this can happen in periods depending on the quality of the chromium itself; however, it has been shown that accidental influences were operating in this instance.

I myself was puzzled by the above sentence, that something *else* can happen than is expected, when studying passivity, though all conditions of the expected phenomenon are not fulfilled, and nothing at all should happen according to foregoing considerations. I have written the sentence in view of the passivity of iron in concentrated nitric acid, where the iron is covered by a layer of insoluble iron oxide instead of being dissolved in the ordinary way.

It was clear to me, that I have encountered some tacitly made *assumption* in my considerations, which is not *generally* valid. I have not sought it long, because already 25 years ago I was occupied with considerations, where this assumption did not appear, but then I did not arrive at an application of my considerations.

The considerations made hitherto in the present investigation suppose tacitly such instances, where it is possible to regard the discreet operations or stimuli as equivalent in so far, that every reaction possible at a *cross-road* requires the same number of them; thus it is entirely irrelevant ^{in which order} ~~where~~ we begin in performing them. But this assumption can be sometimes erroneous, e. g. then, if some suppositions *exclude* each other *altogether*, as the conditions in the reaction of iron

I have to mention also, that in my considerations given above there is concealed *one more* tacitly made *supposition*, namely that the substances considered contain a sufficient amount of their *own energy* in appropriate form for our reactions to be possible without a supply of suitable external energy, e. g. voltaic current, exposure to radiation of a proper quality etc. Also here we shall have to distinguish continuously variable quantities (*actions*) from the mere *stimuli*, as e. g. electric or other sparks, sound-waves, or impacts of any kind; we may recall to mind the latent photographic image and similar instances, where the expended energy is in *no* unambiguous relationship with its effect on the matter capable of reaction, so that we use to be surprised by the want of proportion between both of them. One single spark can ignite an unlimited amount of an explosive and destroy a whole town.

Generally it is evident, that man can act upon a substance only by means of *matter* or *energy*, and this gives us also one possibility of discerning the stimuli. I have mentioned above some energy stimuli; about the *material* ones we can say, that besides the *contact of the reagents* we may include among them also the *catalyzers*, internal and external. For an internal catalysis, a component contained in the respective phase suffices, the amount of which, however, is not changed by the reaction; the external catalysis is caused by the neighbouring phase, which itself is not changed chemically.

The action of the external energies may be called an *elevation*, when the amount of the received energy is *proportional* (at least in infinitesimal changes) to the *amount* of the matter transformed. Where there is no obvious relation between energy and amount of matter transformed, the action is a stimulus.

13. Chemistry has rightly endeavoured for a long time and with considerable success to prepare every compound and every element in a state of the highest possible *chemical purity*, because the pre-

with nitric acid. The *concentration* of the acid cannot be in the homogeneous acid low and high *at the same time*; after all, the acid in question is, besides, not entirely pure being contaminated with oxides of nitrogen, which may here act as catalyzers. Also the eventual passivity of iron is a final result of a certain *process*, which requires a definite, though brief time.

In reading the proofs I find that the difficulties are caused by the hitherto prevailing ambiguity of the word passivity, which in the instance of iron does not accord with my above-cited definition. I have also overlooked, that it may be important, in which *order* the chemist applies his interventions (*actions* and *stimuli*), because the stimulus must be often the last of them.

sence of any unknown component involves a possibility of unforeseen chemical reactions and thus also a possibility of different failures and errors. These last are made especially in seeking components of a substance not yet investigated, be the research undertaken for an analytical or a preparative purpose.

The prescriptions for chemical work are distinguished in general by a great exactness, otherwise the practice would soon discover their imperfection.

Up to now *theory* was not aware of the undeniable fact, that generally the *contact* of the necessary substances is not the *only* condition of the reaction. In chemical equations *only* such substances are named, the amounts of which are changed by the reaction, whereas the other conditions are mentioned only in the text of the explanation. Thus sometimes the influence of substances is often *overlooked*, the amount of which is *not changed* in the reaction, e. g. the influence of the solvent.

Worse still, that during half a century many chemists denied the possibility of *catalysis*; it was ascertained quite definitely by ~~Liebig~~ *Bergelius* and Schönbein, but not before Ostwald was the right place in chemistry assured for it. In spite of this it remains for many up to the present an isolated and therefore mysterious phenomenon. Catalysis as a very often necessary and therefore very frequent *stimulus* naturally accords well with my views.

14. The cooperation of the chemist in the control of possible reactions is realized just by his *selecting* the substances which he allows to change chemically and by reducing the number of substances to a necessary minimum in every instance. If he would not do it, *accidental* causes would decide, what will happen, e. g. a mere stirring up of a heterogeneous mixture of different initial substances.

We may say figuratively, that we often see matter hesitating, in what direction it would go, but the chemist knows, how to bring about the decision by his interventions. Here it is opportune to mention also a reverse phenomenon; a chemist having a sufficient knowledge of his department is able to determine the *future* of his substances, but he can only to a very slight degree disclose their *past* from their present state. A mixture of water-vapour, and carbon dioxide for instance could originate chemically either by combustion of carbon and hydrogen with oxygen, or by combustion of carbon monoxide and hydrogen with addition of water. Besides this, there is a multitude of *organic substances*, which burnt with oxygen give carbon dioxide

and water. The proportion by weight of both products of combustion is usually different and permits often to recognize the burnt substance, but this recognition would be ambiguous with isomeric substances or with mixtures, and becomes possible only with the aid of additional evidence.

15. We have seen, that the prevailing theory of chemical phenomena acts very arbitrarily in judging about the *actual direction* of reactions, but the direction of a reaction has such an importance for chemical practice, that attempts were made since long ago to foresee it with the aid of the doctrine of chemical affinity, though with little success.

Starting from Carnot's views, *thermodynamics*, called also the second law of the mechanical theory of heat (Clausius, Thomson, Rankine, Massieu, Gibbs, Duhem and others), developed in the second half of the past century (beside the still rather new doctrine on the conservation of energy). Thermodynamics teaches, that in all natural processes *entropy increases*, where entropy is a mathematical quantity which can be defined precisely only for reversible processes, these being only limits of actual processes. Though there is no doubt, that the doctrine of the increase of entropy is valid in its whole extent also for chemical phenomena, considerable difficulties are involved in its application in chemistry, because we succeed only exceptionally in determining the differences in entropy between the initial and final state of the substances considered.

A part of these difficulties has been removed successfully by Nernst assuming, that all chemical energy at the zero point of absolute temperature is to be considered as "*free*" energy. The term "free" energy was introduced in thermodynamics by Helmholtz, the very idea having been conceived already by Gibbs (1878), some years earlier.

To be brief in the following explanation I mention, that Gibbs formed four different functions out of the following terms:

1. internal energy of a body,
2. product of absolute temperature and entropy,
3. external work = pressure multiplied by volume.

These functions are especially convenient for solving physico-chemical problems, but each of them in different conditions. It only matters which variables are considered as *independent*;^{*)} I confine

^{*)} Ostwald's translation of Gibbs' work, *Thermodynamische Studien*, Leipzig 1882, p. 105, equations (99) — (102).

myself intentionally to instances in chemistry, where we regard as *independent* quantities only the *components* of a phase, but not their independent "potentials" (of Gibbs).

The quantities: entropy and absolute temperature can be comprised together as *thermal* quantities, the quantities: pressure and volume as *work*-quantities. Practically no other kinds of energy are considered in Gibbs' work than these three: heat, work and chemical energy.

According to Gibbs we can choose the independent variables so, that one of them is a *thermal*, the other one a *work*-quantity; suitable combinations of the independent variables are thus:

1. entropy, volume, components
2. absolute temperature, volume, components
3. entropy, pressure, components
4. absolute temperature, pressure, components.

In the first instance a suitable thermodynamic function is the internal energy itself, in the second one a function, which is obtained by subtracting the product of absolute temperature and entropy from the internal energy (Helmholtz's free energy), in the fourth instance a function, formed by adding the product of pressure and volume (or the external work) to the free energy (Duhem's thermodynamic potential). The function suitable in the third case, namely the sum of the internal energy and the product of pressure and volume, was called recently by G. N. Lewis the heat content.

The *independent* variables in any of these functions we may, of course, always consider as constant, regarding only the independent variations of composition, which obviously may be also constant.

It will be often possible to speak of the thermodynamic functions and of the thermal and work-energy without determining, which combination of the independent variables we have in mind; the reader will have to choose for himself the independent variables and the appropriate function.

Every kind of energy considered here appears as a product of two quantities, one of which is regarded as independent; Gibbs has shown, that choosing properly the respective thermodynamic function we can determine the second quantity simply as the partial derivation of that function or (geometrically) as the tangent in the correctly chosen plane parallel to two axes.

This is the reason, why Gibbs' functions are superior to others.*)

*) l. c., p. 105 (foot-note).

16. I cannot omit here the remark, that in pure chemistry the coupled ideas "independent and dependent quantity" do not occur at all and the chemists use to know them only from the study of other branches; this is probably the cause, why the consideration of the experimenter's *activity* could have disappeared so completely from chemistry, that it is necessary to-day to demonstrate to chemists quite emphatically, that the cooperation of the chemist with nature in chemistry is entirely indispensable, in the laboratory as well as in the factory. A mathematician could never forget so completely, how much of his own *will* is conceded to him for the *free* determination of certain quantities by the mathematical problem just chosen, and the same may be said analogously of a physicist. In chemistry always this or that is going on, but in never enters into anybody's mind, what is man's own share in nature's actions.

This manner of thinking was obviously entirely strange to Gibbs, as far as he was occupied by mathematical or physical considerations, where he was saved from committing an error just by both the notions "independent" and "dependent". He laid stress on them even in the chemical part of his investigations, but the chemistry of fifty years ago could not give him any appropriate instruction on the number of *discontinuities* which are to be taken into account when studying chemical problems; indeed, chemistry cannot do this even to-day.

A genius like Gibbs could have easily constructed from this a perfect theory of all chemical phenomena, but without the knowledge of the accurate number of the discontinuities he could not but stop on the half-way. He avoided all problems, which are *specifically* chemical, and confined himself to only some of them (e. g. dissociation, galvanic phenomena, chemical changes connected with capillarity), which he could solve in spite of the mentioned inadequacy.

Nevertheless he recognized the importance of *catalyzers* and also that of *stimuli* like sparks etc.; some of the discontinuities he reduced to possible differences of his »fundamental equations« valid for different phases, but still it seems to me, that he sometimes was embarrassed by troubles caused him by chemistry of that time, the origin of which he did not succeed in discovering. I feel it today quite plainly in reading all paragraphs of his work, which concern especially chemical questions: particularly, where he is speaking about »possible« chemical phenomena;*) there his exposition, otherwise always very

*) l. c. p. 69—74, 164—171.

concise and clear, evidently suffers from vagueness of the chemical conceptions about, what is »possible«. He might have *felt* well, that the realization of a process can depend on the fulfilment of *several discreet* conditions; but as long as one of them is not fulfilled, we can say with the same right, that the process is »possible«, as well as that it is »impossible«, because in this instance the possibility as well as the impossibility have *different degrees*. The process is absolutely *impossible*, if there is not even one of the conditions fulfilled, it is „possible“, if the first condition is fulfilled, »more possible«, if also a second condition is satisfied, etc., until the last condition is fulfilled. Then, of course, it becomes a *real* process, — if it is »possible« at all under the given conditions. This logical confusion arises just through the idea of »possibility« being too indeterminate without the *gradation* or *discontinuity* in the instance of several (may be only three) conditions, especially when studying thermodynamic equilibrium, where even the »most possible« process *does not go on*. Gibbs, however, confined himself to »possible«*) processes, and the vagueness of this notion was thus transferred automatically to the conception of the thermodynamic *equilibrium*, where *nothing* is going on.

Just about the *number* of the different degrees of possibility chemistry could not tell him *anything reliable*.

I consider the revision of the ingenious investigations of Gibbs on thermodynamics in the just indicated direction as my next task; in this communication I shall mention only some of the preliminary preparations undertaken with this aim in mind.

17. I was using the word »rest« consequently already in all my above considerations aiming at an elucidation of the new chemical notion »stimulus«. The chemical *operations* are divided naturally into *actions* and *stimuli*. The actions can be expressed by means of *independent variables*, but not the *stimuli*, because there is no definite relation between their magnitude and the magnitude of their effect upon the chemical state of the matter in question, the variation of these magnitudes being not *continuous*.

Each individual state in itself is a variety of as many dimensions as there are *actions*; how many dimensions we admit for the quantities dependent on the actions, is really arbitrary, but Gibbs has shown, that in general one single dependent variable with a suitably chosen thermodynamic function suffices, because then we can determine the values of the other important quantities by simple differen-

*) l. c., p., 69 above.

tiation, or geometrically by drawing a tangent correctly. We can speak of an *equilibrium* state of a substance (or several substances) only in so far, as no *stimuli*, or at least no *new* stimuli are intervening; *contact* stimuli supposed to exist in a system are, of course, admissible, but not any changes of their number, except on the external boundaries of the whole variety, for these boundaries mean a new kind of discontinuity. In chemistry it is risky to call every final state an equilibrium state, if it can often be changed into a chemical action without the influence of *external* energy by a mere addition of a bit of a catalyzer or by a spark. Therefore I now prefer to speak of a final state of *rest* instead of an equilibrium state. A present state of *rest* can be followed again by a process ending in a new state of rest; this, however, cannot proceed *for ever*, but only in a finite number of steps. Since in chemistry the present state of a certain substance (or substances) can, under the influence of stimuli, go over into another state, which appears again as a *variety* depending on external *actions*, and since again there is another state of equilibrium possible, it is necessary to distinguish these possible, but evidently diverse states of equilibrium by an appropriate name, e. g. as the chemical states of *rest*. Thus confusions will be prevented, which can be caused, especially in chemical problems, by calling *equilibrium* states those, which are fundamentally different; an equilibrium state is a special instance of a state of *chemical rest* and these may be many. Moreover, a state of chemical rest can be connected with physical changes of temperature and work.

A more detailed elaboration of this idea requires, however, abandoning the chemical notion of a *phase component*; this notion is unsuitable even for the reason, that it was shown to be considerably vague at the very beginning of this communication. *How* it can be changed without affecting the chemical experiences on *elements*, will be dealt with in a further investigation of mine and is after all already rather evident from my "Chemistry of phases".*)

The chemical *rest* is quite well consistent with a physical *unrest*, and physical *unrest* with a simultaneous chemical *unrest*. On the contrary, however, the physical *rest* cannot be consistent with a chemical *unrest*, even then not, if the chemical change would not be connected with changes of energy.**) The chemical rest is well con-

*) "Chemie fází" by Prof. F. Wald, edited as a booklet by the *Česká Akademie věd a umění*, Praha, 1918.

***) Hither belongs perhaps the stereoisomerism.

sistent with the physical one, and then we have a "thermodynamic equilibrium", as far as the intervention of stimuli is excluded and only infinitesimal reversible changes of the independent variables (i. e. actions with the exclusion of *stimuli*), whether material or energy changes, are permitted.

A natural contrast to every rest is unrest, process or *commotion*.

The following proposition can be made basis of the whole thermodynamics:

"No commotion lasts for ever."

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1909 Chemie řáží. Čes. Akad.

Tyto separáty má Dr Antonín Šimek, profesor české university, Brno,
ulice Frant. Bílého 17 -

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Vám, velmi vážený pane inženýre,
v přátelské úctě oddaný