than the former. Now, since Baly's theory is built up primarily on such "opening-up by solvents," it seems remarkable that his experiments are based on the very method which cannot readily show "opening-up by solvents."

It may be maintained that, by changing the concentration of solutions and viewing these in equal thicknesses, spectra are obtained which show the progressive influence ("opening-up") of the solvent. However, attention must be called to the possibility that, even when the solute is not modified by the solvent, such solute molecules themselves may influence the rays of light in some manner similar to finite *masses;* that is, a *grouping* or *clumping* of solute molecules in concentrated solutions and a *thinning-out* by dilution may be factors in absorption phenomena.

Summary.

1. Baly's theory, "the force-field theory," is given as an explanation of chemical reactivity and other chemical phenomena.
2. This theory is based entirely on light-absorption phenomena, the true nature of which is unknown.
3. Baly's experimental methods have often been modified during the past decade but give little confidence of value for the establishment of his theory. As "proofs" of his theory the experiments are too limited and almost entirely unconvincing.
4. Drawing definite structural or dynamic conclusions from absorption phenomena is unwise; grounding a comprehensive chemical theory on the same is too speculative to serve any useful purpose.

SEATTLE, WASH.

A REPLY TO DR. DEHN.

BY E. C. C. BALY.

Received October 11, 1915.

History always repeats itself. Whenever any man has been bold enough to put forward new views involving something more fundamental than the average, the Tories of the time held up their hands in horror at his daring, and his sacreligious attempt to destroy the sacred temples of their faith. Somewhat hasty in their condemnation they frequently suffer from a want of sympathetic intelligence and understanding. While very far from suggesting that Dr. Dehn in any way resembles the Tories of history I will endeavor to show that he does not quite understand and that the gift of sympathy is not his.

Dr. Dehn attacks my theory in mass formation on all sides and I am very sensible of the honor done to it. At first, however, he complains that I have modified my original views and do not speak in exactly the same language as in 1906. He even points out that I have employed new methods of work. Such criticism is not seemly from a man of science, who no doubt himself always tries to work under the best experimental conditions and to modify his early views by help of the experience gained from many years of labor.

Turning to the theory itself as presented in my paper I ought first of all to point out (as was done in the original paper) that the development of the theory from the physical side is dealt with elsewhere. This side has fully been discussed also in a recent paper,[1] and in this paper will be found an answer to the majority of Dr. Dehn's objections.

I will restate my theory as shortly as possible. Every molecule considered in a free state has a minimum reactivity. By the supply of energy to a molecule it gains a definite reactivity, and normally speaking it must absorb that energy before it can react. The energy may be supplied by solvent, light, heat, electricity, etc. Dr. Dehn is under an entire misconception when he states that I limit the energy supply to solvent or light. I discussed these two sources in particular because I happened to have experimented with them. Each molecule when it takes in energy always absorbs it in definite amounts. After the absorption of each definite amount of energy, the molecule becomes endowed with a definite specific reactivity. Every molecule therefore can exist in definite phases according to the amounts of energy which it has absorbed. Each of these phases is characterized by a definite vibration frequency of the order of light vibrations, and thus each phase may be recognized by its own absorptive power of light of definite frequency, that is to say by its absorption band. The quantity of energy that must be absorbed by the molecule when existing in any one phase is given on the energy quantum theory by xhv, where v is the vibration frequency characteristic of the phase of the molecule, h is the Planck constant and $x = 1, 2, 3$, etc.

From a chemical point of view therefore, if a molecule is to enter into a reaction it must absorb at least one quantum of energy (hv) and these quanta can be supplied by the solvent, by light, by heat, etc.

The above facts as regards the different vibration frequencies and the reactivities of the various molecular phases I have clearly established by experiment. Dr. Dehn falls into serious errors when he criticizes these experimental facts. He states that since concentration, temperature, etc., have marked effects on absorption bands there must be an infinite number of phases for any given molecule. Such a statement is absurd, because the effects of concentration and temperature on the wave-length of the center of the band are relatively small, while the difference between the position of the bands due to two molecular phases is very large. There is never the slightest chance of one being confused with the other.

Perhaps the most serious error Dr. Dehn has fallen into is over these

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[1] *Astrophys. J.*, 42, 4 (1915).

absorption bands themselves. Had he only read my papers in the *Philosophical Magazine* or had he only studied the general question of absorption bands he would have been saved from this.

By the term absorption band is always meant an absorption band group. When Hartley, Hantzsch, Purvis, or I speak of an absorption band we always refer to the whole band group. In many cases one absorption band can be subdivided into several sub-groups, and again very frequently each sub-group can be resolved into fine absorption lines. I may say once and for all that it is the whole band group which is characteristic of the molecular phase. The fact that there are for example upwards of 400 lines composing the single ultraviolet band of benzene simply shows that there can be recognized 400 closely situated vibrations characteristic of one absorption band group and one molecular phase. Dr. Dehn goes so far as to say that this on my theory would mean 400 different molecular phases. It means nothing of the sort.

The structure of a band group and the origin of the component absorption lines is of some interest, and I think will dispel any lurking doubt on this point. The long-wave infra-red spectrum of a substance shows series of absorption bands. The frequencies of the bands in any series form consecutive multiples of a fundamental frequency. These fundamental frequencies are supposed to be rotational and are relatively small. In each series the intensities of the bands decrease as the series progresses until they become very small. When there are several series there must exist convergence frequencies and at these positions there will again be strong absorption bands, and each such convergence frequency forms the fundamental frequency of a new series, and so on. Clearly therefore the central frequencies of all the absorption band groups shown by a substance, if they belong to one series, should form consecutive multiples of a fundamental frequency. There should also be a constant difference between the central frequencies of consecutive absorption bands, and this constant difference should equal the fundamental frequency of that series.

Now I have examined many substances and in every case where the complete data are obtainable, I find this constant frequency difference between consecutive absorption bands, and, further, that this constant difference equals the frequency of an important band in the infra-red, *i. e.*, the fundamental band of the series. It is these absorption bands in the visible and ultraviolet, due to consecutive multiples of the short-wave infra-red band that forms the basis of the series, that I refer to in speaking of the characteristic vibration frequencies of the molecular phases.

To turn to the structure of any single absorption band group, Bjerrum showed that in the case of bands in the short-wave infra-red region ($\lambda = 1\mu$ to $10\ \mu$) each band consists of a single central absorption line and that there are symmetrically distributed round it lines, the frequency of which are given by $C \pm nK_1$, $C \pm nK_2$, etc., where C is the central frequency, K_1, K_2, etc., are the fundamental frequencies in the deep infra-red, and $n = 1, 2, 3, 4$......etc. I have found that exactly the same holds good for the visible and ultraviolet absorption bands. This I think effectually proves that the band group is to be considered as a whole system belonging to one molecular phase.

Before leaving this physical side of the theory I think it is of some interest that where there are several fundamental series of vibrations in the deep infra-red, each series in all probability arises from a specific atom or group of atoms. Thus I have been able to calculate the absorption system of phenol from those of benzene and water, and I hope shortly, together with my friend, C. S. Garrett, to show that the vibrations of the SO_2 molecule are due entirely to the sulfur and oxygen atoms. Since the reactivity of a molecule depends on the phase it accepts, and since the phase is characterized by a free period of vibration compounded from those due to the constituent atoms, the deductions that might be drawn are suggestive.

I have laid some stress on the physical side of the theory because therein is to be found the proof that different absorption band groups and reactivities of one and the same substance are not due to molecular rearrangement as suggested by Dr. Dehn. As long as the constant frequency difference relation between them holds good all the visible and ultraviolet band groups must be functions of the same primary structure, namely, that primary structure which shows the fundamental infra-red band group.

The foregoing constitutes the fundamental basis of my theory. In order to account for the phenomena I have made use of the conception of the electromagnetic force-fields of the atom as employed by physicists to explain the Zeeman effect, and by Humphreys to explain the pressure shift of spectrum lines. By the application of these atomic force-fields to the molecule I show that all the phenomena of chemical reactivity can be explained. The first result accrues that the so-called affinity is the outward and visible sign of the mutual action of the atomic and molecular force-fields.

Certain other deductions also follow. On the one hand, we have the existence of the molecular phases, such as were foretold from the energy quantum theory; on the other, the mechanism of chemical reaction whereby an intermediate reactive phase must be accepted by any molecule before it reacts. With all due respect to my opponent this last has definitely been proven. The proof is fourfold; firstly, the change in absorption exhibited by a compound, namely, the formation of a new absorption band at the moment before a reaction takes place which disappears when the reaction takes place. Secondly, the fact that the vibration frequency of the new absorption band is the same as that of the fluorescence band of the substance before the change of phase took place. Thirdly, the difference between the frequencies of the absorption band groups shown before and after the change in molecular phase is equal to the frequency of the fundamental absorption band in the infra-red, observed with the pure substance in the absence of solvent. Fourthly, the reaction will not take place at all unless the molecules pass first into the new and active phase. (The remaining deductions as regards catalysis, etc., are so obvious that they need not be referred to.)

I feel that I have said enough to answer the majority of Dr. Dehn's criticisms, namely, those which are based on misconception. No assumption is made that the necessary energy is derived from the solvent or light only. The band groups characteristic of the phases of any one molecule are few in number and can perfectly well be recognized by the constant frequency difference relation. Finally, the complete structure of a single band group as studied by Hartley, Purvis and others must not be confused with the different band groups themselves. Although one band group may consist of many hundred absorption lines, it is the whole group which is characteristic of the molecule.

The remaining criticisms may be dealt with *seriatim* as follows: Dr. Dehn says that the theory is based solely on light phenomena, and that it presents nothing new or useful. After all, the whole of astronomy is based on observations of light phenomena and indeed it is to the great work of Dr. Dehn's fellow Americans that this science owes so much. If there were nothing new in the views I put forward, I believe that Dr. Dehn would not be so troubled in spirit. When he says "nothing useful" then I fear he lacks an intelligent sympathy, for I maintain that my theory, based as it is on the force-fields of atoms so successfully employed by physicists to explain the Zeeman effect and pressure shift of spectrum lines, does make a reasoned attempt to explain many facts of chemistry which are somewhat obscure. I need only mention catalysis and those myriads of intermediate molecular compounds he refers to which are recognized but not explained by chemists.

I make no attempt to demonstrate the existence of the force-fields, but only to prove the existence of phenomena which the application of the physicists' conception of force-fields to chemical reaction leads one to expect.

Dr. Dehn again misunderstands me when he says that I assume that every change of absorption indicates a change in chemical composition. I do nothing of the sort. The change in absorption whereby a previously latent free period of vibration is called into play is due to a change in the molecular force-field produced by the addition of one or more energy quanta supplied by light, heat or solvent, etc. The chemical composition is not changed but only the reactivity.

Dr. Dehn lastly quarrels with my use of the phrase residual affinity. He apparently views residual affinity as being only the property of molecules which are unsaturated as regards the primary valencies of the atoms composing the molecules. I plead guilty at once to the use of the phrase in a far less restricted sense. Every chemist of the present day must surely recognize the possession by compounds, saturated as regards their primary valencies, of properties which may best be classified as residual affinity. Whether these properties are attributed to secondary valencies or to any other cause, the properties exist and it is these that I speak of as residual affinity and define as the residuum of affinity which is left after the force lines of the atomic fields have condensed together with the maximum possible escape of energy. It is to this escape of energy that the heat of reaction may be traced. No chemical theory can exist without affinity although there seems to be no satisfactory definition or explanation thereof. I have ventured to show that in the electromagnetic force-fields of the atom as devised by the physicist an explanation can be found. *Hinc illae lachrymae.*

THE UNIVERSITY, LIVERPOOL.

[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY, PRINCETON UNIVERSITY.]

A CALOMEL STANDARD CELL.

BY G. F. LIPSCOMB AND G. A. HULETT.

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Experimental investigations on standard cells have been confined mainly to two combinations, the Clark cell and the Weston cell. These have been characterized by their reproducibility and their constancy, while other combinations which have been studied have proved lacking in these characteristics. For the construction of standard cells it has been found necessary to employ liquid electrodes, owing to the inconstancy of potential shown by a metal in the solid state against a given solution, so mercury and amalgams are used. Further, it is necessary that the base metal exist in only one state of oxidation and well removed from mercury in the electromotive series. The salts of the base metals should be well defined and be quite soluble. It has been assumed that the depolarizer must possess a certain solubility which must not be too small, since mercury has shown a constant potential only against the electrolytes which contained reproducible and constant amounts of mercury in solution. This idea has been regarded as militating against the employment of mercurous chloride as depolarizer. On the other hand, if the solubility be too great, as in the case of $CuSO_4$ of the Daniell cell, diffusion of the depolarizer may take place, and cause inconstancy of the cell. With