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BALY'S THEORY OF CHEMICAL REACTION AND REACTIVITY.[1]

BY WILLIAM M. DEHN.

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This theory, developed since 1904 from voluminous spectrophotometrical studies,[2] is presented in full in the May number of THIS JOURNAL.[3] After perusing this and previous contributions one sees that the author has based his theory solely on light phenomena of the ultraviolet region[4]

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[1] [Observe Baly's reply following. This criticism of Baly's theory was submitted this summer to Baly by the editor; Baly's reply was also submitted to me by the editor. My additions and counter-replies are all included in brackets, mostly contained in footnotes of this contribution.]

[2] *J. Chem. Soc.*, **85**, 1029 (1904); *Z. physik. Chem.*, **55**, 485 (1906); *J. Chem. Soc.*, **87**, 766, 1332, 1347, 1355 (1905); **89**, 489, 502, 514, 618, 966, 982 (1906); **91**, 1122, 1572 (1907); **93**, 1747, 1808, 1902, 2108 (1908); **95**, 144, 1096 (1909); **97**, 571, 1494 (1910); **99**, 856 (1911); **101**, 1469, 1475 (1912); **103**, 91, 2085 (1913); **107**, 248 (1915); *Phil. Mag.* [5] **49**, 517; [6] **2**, 386; [6] **27**, 632 (1914); [6] **29**, 223 (1915); *Astrophys.*, **42**, 4 (1915).

[3] THIS JOURNAL, **37**, 979 (1915); *J. Soc. Chem. Ind.*, **34**, 393 (1915). [See also *Astrophys. J.*, **42**, 4 (1915), in which Baly claims (in the reply following) to have anticipated and met the objections advanced here.]

[4] ["It is surprising that in all the work that has appeared dealing with the absorption spectra of organic compounds in relation to their structure, no notice has been taken of the absorption exerted by these compounds in the infra-red region of the spectrum..... it has been attempted entirely to decide the constitution from arguments based on ab-

of the spectrum, consequently one hesitates to accept so sweeping[1] a theory, especially when it is remembered that in no case[2] has the true relation of spectrum-absorption figures to chemical structures or energies[3] been demonstrated. Furthermore, when it is remembered that Baly has made purely physical studies[4] of compounds prepared by his colleagues or by Kahlbaum, and thus he himself has made few original *chemical* observations; or, when it is remembered that Baly presents a theory of chemical dynamics based solely on statical[5] chemical experiments, one wonders at this invasion of the province of pure chemistry and at this attempted destruction of so many of her sacred temples.

By way of anticipation, it may be stated that, stripped of its novel[6] and figurative language, Baly's theory of chemical reactivity appears vague and speculative and presents nothing new or useful. Tested by his own data,[7] it is observed that this theory rests on insufficient experimental evidence[8] and often on inaccurate observation.[9]

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sorption in the ultraviolet and visible regions alone." Baly writes this (*Astrophys. J.*, **42**, 5 (1915)), yet he is the greatest offender in this respect, for he has made many spectrometrical studies, all in the ultraviolet region, and has attempted to draw more, varied, and speculative conclusions than any other author.]

[1] See summary, This Journal, **37**, 993. [Observe that Baly's theory renders obsolete LeBel and van't Hoff's theory of stereoisomerism; it relegates to oblivion all chromophoric-group theories of color; "it affords a reasonable explanation of allotropy, magnetic rotation, stereoisomerism, optical rotatory power....the phenomena of isomerism as a whole," of chemical reactivity and reaction, hydrolysis, catalysis and photocatalysis, also of such light phenomena as absorption, fluorescence, phosphorescence. If Baly is not a humorist, he richly deserves the sympathy which he seeks. (*Loc. cit.*)]

[2] [It will be observed that no such case is attempted to be given in Baly's reply following.]

[3] It will be shown below that it is not necessarily true, as Smiles states ("The Relations of Chemical Constitutions and Some Physical Properties," p. 361). "The relations between absorption and constitution must be sought in the dynamic condition of the valencies of the absorbing group."

[4] [In the reply following, Baly occupies more than half of the space in discussing new physical data not published by him when his theory appeared in This Journal (see *Astrophys. J.*, **37**, 4 (1910)). However this added matter does not appear relevant to the discussion of *chemical reactivity*, though it may throw some new light on the interrelation of absorption, fluorescence and phosphorescence, for a *multiple* relation of these light phenomena may be as independent of chemical reactivity, as the periodicities of sound waves or as the sound waves themselves, are independent of the chemical affinities of the substances which transmit such sound waves.]

[5] See below.

[6] Among earlier papers we find such novel phrases as "nascent carbonyl group" (*J. Chem. Soc.*, **89**, 491 (1906)), "pseudo-nascent" (*Ibid.*, **89**, 492), "chemical reactions in embryo" (*Ibid.*, **101**, 1471 (1912)), etc.

[7] [Much of the data given in this criticism to show the inconsistencies of Baly's theory have been taken from Baly's own papers.]

[8] [See especially This Journal, **37**, 987–988 (1915); *Astrophys. J.*, **42**, 12–16 (1915).]

[9] [See especially Baly's studies on benzene (*J. Chem. Soc.*, **87**, 1332 (1905)). Com-

Though modifying his views, theories[1] and methods[2] as new conditions arose during the past decade, Baly has clung tenaciously to one phrase, "the open and closed force-fields." This he offers as *the* explanation of chemical reactivity and most other chemical phenomena.

However, it may be stated at once, if the old terms *chemism, chemical affinity, chemical potential,* or *chemical intensity* be re-substituted[3] throughout for "force-fields," whose true nature, of course, remains unknown, it is observed that no new light is thrown on chemical reactivity. With this and with other terms, one cannot escape the impression that Baly is clothing familiar concepts in new language and it scarcely needs to be

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pare with Hartley (*Proc. Roy. Soc.*, 80, 162 (1907)) or see also Kayser's "Handbuch der Spectroscopie," Vol. III, pp. 483–5.]

[1] It is interesting to find in Baly's later papers no reference to the word *isorropesis,* coined by him (*J. Chem. Soc.*, 89, 498 (1906)) and used in a series of papers to designate "potential tautomerism." In the words of Baly and Desch (*Ibid.*, 87, 768 (1905)): "No organic substance shows an absorption band unless a possibility of tautomerism exists in the molecule." The dynamic changes of such tautomeric parts of molecules were described by the word "isorropesis;" that is, isorropesis is the cause of absorption bands. In Shephard's recent text-book on "Photochemistry," p. 189, we read: "Baly's theory of isorropesis......at once begs and solves the problem."

[It would be interesting to know if Baly still believes in his isorropesis theory. It and his present theory to account for absorption phenomena are different, if not contradictory; hence, at least for the purpose of clarification of the literature (see especially the Ramsay series of text-books on physical chemistry), it would be fair to withdraw this earlier theory, if it is no longer tenable. So also in respect to the theory of vibration of the benzene ring, a theory based on coincidental relations of carbon linkings in the molecule and absorption bands in a limited portion of the spectrum (Baly and Collie, *J. Chem. Soc.*, 87, 1332 (1905); 89, 514 (1906)). See also Hartley (*Ibid.*, 87, 1826 (1905)). If this theory also is untenable, why not withdraw it? If the earlier theories were incorrect, what salvage can be expected to be made from the present speculations?]

[2] Until recently the iron arc was used by Baly as the source of light in his spectrophotometrical studies. Now he uses arcs containing salts of cadmium, uranium, and molybdenum. (Compare *J. Chem. Soc.*, 85, 1029 (1904) and 99, 856 (1911).) [If the earlier experiments involved errors resulting from imperfect illumination, what confidence can we place in conclusions drawn from these earlier experiments? Baly's chief support for his theories is based on experiments involving use of the iron arc (*J. Chem. Soc.*, 93, 2108 (1908); 101, 1475 (1912); THIS JOURNAL, 37, 987–88; *Astrophys. J.*, 42, 12–16). Why not reinvestigate with the modern arc? What assurance have we that the present methods also do not contain errors? If spectrometrical methods are not at present absolutely reliable (like the use of balance) how can such spectrometrical studies be made the experimental basis of a theory that comprehends and explains all chemical phenomena?]

[3] [Does Baly intend that the energies, chemical affinity and opened-up force-fields are the same and may be taken synonymously? If conceived to be different, does Baly consider himself to have discovered a new force of nature? Does Baly conceive of the successive opened-up stages of force-fields to be portions of the total chemical affinity?]

remarked that the paraphrasing of a concept no more adds new information than does transliteration or translation of the same.

Let us note some other definitions of Baly. *Residual affinity*[1] is defined as "the uncompensated balance of force-lines," or "uncompensated residuum when the maximum possible condensation of force-lines of the molecule has taken place."

Valency[2] is defined as a "resultant effect of force-lines," or "interatomic rearrangement of electrons when the potential gradients within the additive complexes first formed are sufficiently steep," or "transference[3] of one or more electrons along the potential gradients which is set up by the condensing together of the force-fields arising from the electromagnetic fields of two atoms of opposite type."

A *chemical reaction*[4] "between molecules depends on these force-fields. . . and will occur only when the gradient within the complex first formed is sufficiently steep to cause the electrons to migrate."

It appears[5] that "shallow and steep potential gradients" are only less and greater chemical reactivities. It would seem also that Baly's own force-fields have "been invoked to play the rôle of *deus ex machina*[6] and relieve the exigencies of the situation."

When we inquire further what Baly's conception of force-fields is, we find[7] "each atom. . . .is the center of a field of force, the lines of which radiate in every direction." Elsewhere we read[8] that these force-fields "have been proven to exist in the immediate neighborhood of the atoms." Compounds also are supposed to have force-fields which are so complex that they present a veritable "net-work[9] of potential gradients."

Now though it may be possible to demonstrate the existence of "force-fields" such as Baly describes, certainly his experiments have not demonstrated them, indeed, his experiments have not necessarily indicated

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[1] [THIS JOURNAL, 37, 982 (1915); *J. Chem. Soc.*, 101, 1469 (1912). Observe the last paragraph of Baly's reply following: "Every chemist of the present must surely recognize the possession by compounds, saturated as regards their primary valencies, of properties which may best be classified as residual affinity." I beg of him to present some one *chemical* property of hexane, of any paraffin hydrocarbon, or, indeed, of any *saturated* compound, that can or must be referred to residual affinity such as he describes.]

[2] THIS JOURNAL, 37, 983 (1915); *J. Chem. Soc.*, 87, 784 (1905); *Astrophys. J.*, 23, 110. Baly's earlier conception of valency seems to have been elastic tube-like structures.

[3] THIS JOURNAL, 37, 980 (1915).

[4] *Ibid.*, 37, 981 (1915)

[5] *Ibid.*, 37, 983-4 (1915).

[6] *Ibid.*, 37, 982 (1915).

[7] *J. Chem. Soc.*, 101, 1469 (1912).

[8] THIS JOURNAL, 37, 982 (1915). Perhaps no one denies that all atoms possess energies or forces usually called chemical affinity.

[9] THIS JOURNAL, 37, 986 (1915).

the probability of such "force-fields." This will become evident when examination is made, especially of the mode of "opening and closing" of such "force-fields."

That it may be shown at once that the *modus operandi* of "force-fields" is vaguely conceived and Baly's whole theory rests on insufficient observation and experiment, a quotation[1] from his summary is made. "To the closed force-fields and their opening-up by the influence of solvents or light may be attributed all phenomena of chemical reaction." Evidently Baly conceives of *light* or *solvents* or both as the only causes of such "opening of closed force-fields" (chemical reactivity). Apparently he overlooks heat,[2] pressure, electricity and other dynamic causes of chemical reaction. This oversight is remarkable since to the chemist, *heat*, in the presence or the absence of solvents, is far more important than light[3] in promoting chemical reactions. By way of an example it needs here only to be recalled that nearly all organic substances are decomposed at high temperatures, consequently "force-fields" must be opened by heat also.

It must not be denied that the validity of his theory possibly may be established on the basis of study of solvents and light only. However, a theory which is claimed to be a fundamental explanation of "all the phenomena of chemical reaction" certainly must include all "openers" of chemical reactivity.

Now, Baly conceives[4] of these force-fields to be "more or less closed"

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[1] THIS JOURNAL, **37**, 993, also p. 984 (1915).

[2] Perhaps the observation (*J. Chem. Soc.*, **101**, 1475 (1912)) that "the vapors of ammonium chloride and mercurous chloride.... possess force-fields so condensed that increase of temperature alone is not sufficient to open them," has led Baly to believe that all force-fields are resistent to opening by heat.

[3] It is not clear whether Baly believes that chemical reactions may take place in the dark. Certainly it follows as a corollary from the quotation above that substances not in solution would not react in the dark. Some discussion of reactions in the absence of light is given by Baly. (See *J. Chem. Soc.*, **87**, 1333 (1905).) [See Baly's most recent paper (*Astrophys. J.*, **42**, 8 (1915)), wherein he again states that the unlocking of chemical affinity "may be brought about in one of two ways: namely, by the use of a substance possessing residual affinity or by the action of light." See now Baly's reply following, wherein he acknowledges *other* dynamic causes of chemical reaction. Note here also, by the way, the following: "Every molecule considered in a free state has a minimum reactivity....it must absorb....energy before it can react....at least one quantum of energy." "However, there are known to chemists so many experiments wherein chemical reactions take place spontaneously, without the application of energy, without the medium of a solvent and, indeed, *give off energy*, that this new conception of Baly is surprising, to say the least."]

[4] THIS JOURNAL, **37**, 982 (1915). See Mellor's "Statics and Dynamics," Chap. VI, for a discussion and bibliography on the "period of induction." Evidently what Baly calls "closed force-fields" has been known since the beginning of the nineteenth century. [Perhaps the best characterization of Baly's theory is that he has rediscovered chemical affinity.]

but, being opened, "the previously closed fields become endowed[1] with reactivity." Moreover, "the opening-up of a complex field must take place in definite stages[2]. . . .called into play by the use of suitable solvents" and "if the opening-up process is carried to the farthest possible extent. . . . ionic dissociation[3] is the sequence."

The state of affairs thus indicated would necessitate *ex hypothesi* different affinity constants for the same substance as the successive stages were opened up and yet other affinity constants for the same substance in different solvents,[4] propositions impossible to demonstrate and conditions difficult to conceive of, especially when solutes are contained in non-ionizing media. Furthermore, since changes of concentration, pressure and temperature[5] have marked effects on absorption bands, various other stages,[6] indeed, an infinite series of stages, must be assumed. Now Baly would have us believe "each stage is characterized by its light absorptive power[7]. . . .and each stage possesses a definite reactivity," therefore, we must assume not only an infinite series[8] of absorption curves but an infinite series of reactivities and consequent reactions and products. These results, of course, are contrary to fact,[9] contrary to the chemist's conceptions of valency, and contrary to the fundamental laws of definite, multiple, and equivalent proportions.

[There can be no quibble that Baly believes that molecules plus energy coincidentally and inevitably cause: (1) "opened-up stages," (2) chemical reactivities and (3) "definite vibration[10] frequencies." Now if chemical reactivities and spectral phenomena are co-existent properties, all molecules showing definite vibration frequencies must show chemical reactivities and all chemically reactive molecules must show definite vibration frequencies. That the former of these is not necessarily true is proven by the inert gases helium, argon, etc., which show definite vibration frequencies but no chemical reactivities. On the other hand, that

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[1] THIS JOURNAL, **37,** 984 (1915).

[2] *Ibid.*, **37,** 986 (1915). See also *J. Chem. Soc.*, **103,** 2086 (1913). "We have now succeeded. . . .in recognizing several distinct stages."

[3] THIS JOURNAL, **37,** 985 (1915).

[4] See the various absorption curves of acetoacetic ester and ethoxycrotonic ester in different solvents (Hantzsch. *Ber.*. **43,** 3058–9 (1910); Baly, *J. Chem. Soc.*, **85,** 1034–9 (1904)).

[5] Kayser's "Handbuch der Spectroscopie, Vol. III, pp. 128–141; see also studies by Purvis. In the reply following, observe how Baly treats this objection.

[6] Baly and Krulla, *J. Chem. Soc.*, **101,** 1472–3 (1912).

[7] THIS JOURNAL, **37,** 987 (1915).

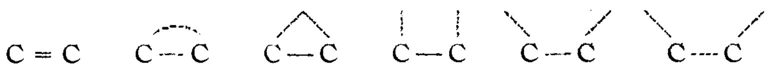
[8] See for instance some of Baly's curves (*J. Chem. Soc.*, **85,** 1039). Varied quantities of hydrogen chloride will give curves covering the entire area between the upper and the lower curves, hence an infinite number of curves.

[9] [As acknowledged by Baly in his reply following.]

[10] [See THIS JOURNAL. **37,** 993 (1915); also Baly's reply following.

all chemically reactive molecules cause definite vibration frequencies is not only undemonstrable but improbable. This improbability is shown: (1) by the fact that certain molecules react in the dark without developing light phenomena and (2) by the *non-proportionality* of chemical reactivity and vibration phenomena: (*a*) certain solids and colored substances may show considerable spectral activity but little or no chemical reactivity, (*b*) the most chemically reactive substances are not necessarily the most active spectrally. In this connection it may be stated that, since Baly now acknowledges *heat* to be an "opener of chemical reactivity," it may be easier for him to understand that light frequencies may possibly be independent of chemical reactivity.]

At this time it must be observed that Baly has never indicated by figures what his conceptions are of "stages" of "opened-up force-fields." Since these have been left to our imagination, some visualization of them is not only permissible but necessary. Therefore, we depict them as follows:



wherein each indicated stage and their intermediate forms are assumed (with Baly) to possess specific chemical and light-influencing properties. Though such an explanation is conceivably simple[1] and elastic, it must be remembered that these stages are purely speculative, are contrary to the conventional conceptions of structural chemistry, and, until some proof of their existence[2] is advanced, can serve no useful purpose.

Let us now examine more in detail the "mechanism of the opening of a closed force-field." "If the molecules of a compound,[3] the force-fields of which are closed, be brought into the neighborhood of the molecules of another compound possessing residual affinity, the force-lines of the latter will interpenetrate the closed fields of the former, with the result that they will be opened and endowed with enhanced reactivity.... the case is an absolutely general one."

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[1] Apropos of its claimed simplicity, the following quotation is made: "One advantage of the theory may perhaps be touched upon, namely, it does away with the somewhat alarming complexity which Hantzsch's doctrine of one adsorption curve one structure introduces into organic chemistry." (*J. Soc. Chem. Ind.*, **34**, 399 (1915)). However, note Baly's "veritable net-work of potential gradients" in molecules. (THIS JOURNAL, **37**, 986 (1915).) If imperfect correlation of absorption curves and chemical structures are impossible, thereby (according to Baly) invalidating the quinonoid theories of color, why does not this same imperfect correlation of absorption curves and "opened-up stages" cast discredence on Baly's theory? It must furthermore be remembered that absorption phenomena possibly are independent of specific structures and chemically active groups.

[2] See Baly's reply following, in which he acknowledges his lack of proof: "I make no attempt to demonstrate the existence of the force-fields."

[3] THIS JOURNAL, **37**, 396 (1915).

Here and elsewhere in Baly's papers we are led to believe that the residual affinities of the solvent open up the force-lines of the solute, But, by way of an example, let us consider *hexane, a saturated compound not possessing residual affinity.* Judged by its light-absorption curves,[1] solutes are affected by hexane in the same manner as by other solvents which are held to possess residual affinity. Hence it cannot be maintained by Baly that in all cases the force-lines of the solvent open up, interpenetrate, and endow solutes "with enhanced reactivity," neither can it be maintained that such changes in absorption spectra as result from dissolving substances in hexane are brought about by the residual affinities or "force-lines of the solvent."

Further, Baly dogmatically states[2] "that addition complexes between solute and solvent, usually known as solvates....always exist when such molecular types are brought together." However, it must be remembered that with paraffin hydrocarbon solvents this is impossible, since these compounds are saturated,[3] possess no residual affinities and have not yielded such molecular compounds.

Nevertheless, let us see what two experiments Baly[4] gives to "prove the existence of....intermediate stages" which he claims "afford proof of the force-field theory."

The aminobenzaldehydes are[5] nearly colorless or yellow substances giving one absorption band in alcoholic solution; with a little hydrogen chloride their alcoholic solutions, but not their aqueous solutions, are more deeply colored and give two absorption bands; with an excess of hydrogen chloride, their alcoholic solutions become colorless and show one band. All three absorption curves are different.[6] Now to account for the second absorption band and the increase of color, Baly[7] *assumes an "intermediate form which reacts with more acid to give the salt."* In other words, here and elsewhere Baly makes the following chain of assumptions:

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[1] Hantzsch, *Ber.*, **43**, 3058–74 (1910); see also Baly's curves for picric acid (*J. Chem. Soc.*, **103**, 2094 (1913)) which was dissolved in *heptane* and other solvents such as (*a*) alcoholic HCl and (*b*) dimethyl aniline. Observe that all these curves do not differ widely, though heptane is devoid of residual affinity and the other solvents are not.

[2] THIS JOURNAL, **37**, 984 (1915); *J. Soc. Chem. Ind.*, **34**, 396 (1915).

[3] That residual affinities are not necessarily correlated with absorption bands must be concluded from studies of the absorption spectra of paraffin hydrocarbons. See Kayser's "Handbuch der Spectroscopie," Vol. III; methane, p. 529; ethane, p. 263; butane, p. 369; hexane, p. 517; heptane, p. 216; octane, p. 540. It is observed that, while showing absorptive spectra, these compounds are devoid of residual affinity.

[4] THIS JOURNAL, **37**, 987–8 (1913); *J. Chem. Soc.*, **93**, 2110 (1908); **101**, 1475 (1912); *Astrophys. J.*, **42**, 11–15 (1915). The data of these two studies constitute the basis of Baly's theory.

[5] THIS JOURNAL, **37**, 987; *J. Chem. Soc.*, **93**, 2108 (1908).

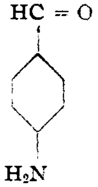
[6] *Loc. cit.*

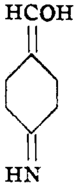
[7] THIS JOURNAL, **37**, 987 (1915).

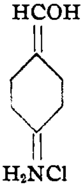
color $\rightleftarrows$ absorption bands $\rightleftarrows$ intermediate compounds $\rightleftarrows$
opened-up stages $\rightleftarrows$ force-fields $\rightleftarrows$ theory of chemical reactivity.

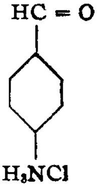
[Baly recognizes here the probable formation of a compound intermediate to *p*-aminobenzaldehyde and its hydrochloride. Even if the existence of this assumed intermediate compound were proved by chemical methods of separation, its existence *per se* would not prove the existence of an "opened-up stage" such as Baly assumes. By way of an example, if ammonia is treated with an excess of an alkyl iodide, quaternary alkyl ammonium iodide is formed as the end product and *six definite intermediate compounds* (the respective primary, secondary, tertiary bases and their salts) are formed. Here no assumptions of opened-up stages such as Baly conceives of are recognizable or are necessary to account for all the phenomena.]

Let us consider how, on the other hand, the above facts can be accounted for by the quinonoid theory:

(a)


(b)


(c)


(d)


Here, of course, two intermediate products are assumed; this[1] quinonoid explanation, therefore, may not be correct; but Baly's explanation also may not be correct, for he also makes two assumptions,[2] and, while so doing, offers the above example as "a definite *proof* of the force-field theory."

Now let us examine Baly's second example[3] which[4] "establishes beyond any doubt the existence of the intermediate stage in a chemical reaction such as was deduced from the force-field theory."

Absorption spectra were taken of *p*-nitroanisole (1) in alcohol, (2) in sulfuric acid and (3) in sulfuric acid after warming. Different curves were obtained in the three cases. Baly states, "we have evidence that the whole of the *p*-nitroanisole is converted into the intermediate phase." This evidence of total conversion or, indeed, of partial conversion is not

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[1] Observe how (*a*) and (*b*) account for the original colorless and colored forms of the compounds. Also observe how Baly's theory fails to account for the original colors. Finally observe Baly's anomalous reaction of the addition of hydrogen chloride to the hydrochloride of the original *p*-aminobenzaldehyde (see *Astrophys. J.*, **42**, 12 (1915)).

[2] These assumptions are: (1) modified absorption figures indicate changes of composition; (2) these changes of absorption and composition indicate molecular addition.

[3] *J. Chem. Soc.*, 101, 1475 (1912).

[4] THIS JOURNAL, 37, 988 (1915).

given in the paper.[1] Now, while not denying that he possesses such evidence, or that an intermediate compound can be formed in this case, it must be remembered that Baly is assuming here that every change of absorption curve indicates a change of chemical composition. That this is true has not been demonstrated; on the contrary, that this is not true, has been indicated by various absorption studies.[2]

Now since the existence of intermediate compounds, in the two cases given, is merely *assumed*, no real proof of Baly's theory is submitted. Furthermore, even though the alleged intermediate compounds could be proven, they would not in themselves, nor would their absorption curves, constitute evidence of "opened-up force-fields," for myriads of intermediate molecular compounds are recognized by chemists without postulating or necessitating a condition of "stages" or "opened-up force-fields."

Let us next consider how *light*, as well as solvents, "open up closed force-fields." Let us see,[3] indeed, "how the whole of the phenomena of photocatalysis can be explained." This explanation follows. "Due as they are in the first place to the rotation of the electrons of the constituent atoms, it follows that the force-fields must be capable of absorbing these rays of light which have the same frequency[4] as that of the electrons. The light in being absorbed does work upon the closed field and opens them, and this gives a rational explanation of the selective absorption of light."

It is observed that this "rational" explanation involves the following assumptions: (1) the electronic composition of all matter, (2) rotation of electrons, (3) synchronous vibrations of electrons and rays of light, (4) transference of some light energy into chemical energy, and (5) consequent maintenance of force-fields in an "opened-up state." It would seem that much light is necessary for all this.

Now while remembering[5] "the primary assumption that there exists a definite correlation between the constitution of a compound and the power which it exerts of absorbing light" or, in other words, while believing with Baly that each absorption line, band, or general absorption area is caused by a different and definite "opened-up stage," let us see what conclusions can be drawn from absorption spectra of pure substances.

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[1] *Loc. cit.*

[2] See the various absorption curves of acetoacetic ester, etc., in different solvents: Hantzsch, *Ber.*, 43, 3057–74; Baly and Desch, *J. Chem. Soc.*, 85, 1034–39; see also Purvis' papers for more rational explanations of absorption bands.

[3] This Journal, 37, 986 (1915).

[4] It is possible that rays of light whose frequencies *differ* from the frequencies of the electrons are the ones that are absorbed. That photochemical substances, so simple as silver halides are sensitive to a wide range of light rays suggests such a possibility.

[5] *J. Soc. Chem Ind.*, 34, 394 (1915); This Journal, 37, 979 (1915).

Consider first the simple substance water. We find[1] that it gives a multitude of absorption lines and bands, hence we must conclude with Baly that it possesses a multitude of "opened-up stages" and a multitude of different reactivities.

Or let us consider benzene. Hartley and Huntington[2] found in the ultraviolet spectrum seven absorption bands; this was confirmed by Baly and Collie.[3] The latter authors demonstrate geometrically that benzene can have only seven "stages," hence a striking "agreement between facts and the theory" is claimed. Now since this illustration is often quoted and is used as the basis of a dynamic theory[4] of the benzene system, it must be recalled not only that liquid benzene itself exhibits numerous bands in the visible and the infra-red regions of the spectrum,[5] but Hartley[6] has shown, when in the form of vapor, benzene gives *eighty-two bands.* It is evident that this theory, based on coincidental relations of absorption bands in a portion of the spectrum, to pulsating linkings or "opened-up stages," must fall.

Notice further what erroneous conclusions may be drawn from a limited portion of the spectrum. On the one hand, we find benzene giving more than seven bands, while, on the other hand, we find naphthalene[7] giving only *three* bands. According to Baly's theory, the latter possessing more structural linkings,[8] should have more bands and more "stages," but such is not the case, hence again the theory is shown to be inconsistent.

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[1] Kayser's "Handbuch der Spectroscopie," Vol. III, pp. 389–399. See Baly's vague discussion of hydration, THIS JOURNAL, **37,** 983 (1915).

[2] *Phil. Trans.*, **170,** 257 (1879). Hartley and Dobbie found only six bands, *J. Chem. Soc.*, **73,** 695 (1898).

[3] *J. Chem. Soc.*, **87,** 1335–6 (1905). Grebe gives eight bands, *Z. wiss. Phot.*, **3,** 376.

[4] *J. Chem. Soc.*, **71,** 1013 (1897); **87,** 1826 (1905); **89,** 514 (1906). Also see Smiles's text-book (p. 383) and other text-books of the Ramsay series.

[5] Kayser's "Handbuch der Spectroscopie," Vol. III, pp. 483–5.

[6] *Proc. Roy. Soc.*, 80, 162; *Phil. Trans.*, **208,** 475 (1908). [In the reply following, Baly quibbles over the use of the term *absorption band.* In this paper I have always quoted and used this term in the sense and words of no less authority than Kayser (and Baly himself). As the result of recent studies, however, Baly would now have us believe "by the term absorption band is always meant an absorption band group." Notice, a *band* is a *band group.* Until these become interchangeably and commonly accepted I must beg to limit my use of these terms to the common usage of the literature. It would be interesting to have Baly state how many absorption bands, absorption band groups and absorption lines the simple compound benzene gives. (See Baly, *Astrophys. J.*, **42,** 32–35 (1915).) Also how many "molecular phases" or "opened-up stages" does benzene possess?]

[7] Baly and Tuch, *J. Chem. Soc.*, **93,** 1902 (1908); Stokes and Soret, *Arch. soc. phys. et nat.*. [3] **9,** 513; Hartley, *J. Chem. Soc.*, **47,** 685 (1885).

[8] Baly and Tuch, *J. Chem. Soc.*, **93,** 1905 (1908). "Naphthalene. . . .consists of two rings of which one is truly benzonoid." See here also Baly's effort to bolster up his isorropesis theory.

Though no good reason has ever been given why all the spectral bands[1] should not be used in studies on the relation of absorption spectra to chemical constitution and chemical dynamics, Baly and others have made use almost exclusively of the ultraviolet region. Recently[2] Baly realizes the importance of infra-red bands for we read: "It would seem obvious that there must be an intimate connection between all the absorption bands exerted by a compound, in whatever region of the spectrum they may occur."

Therefore, while making use of all available absorption lines and bands, let us examine simple and closely-related substances to see if they correlate with dynamic groups, linkings, or "opened-up stages." The following[3] may be taken as typical examples: nitric acid-8; chloroform-15; methyl alcohol-13; ethyl alcohol-13; ethyl bromide-27; ethyl nitrate-10; acetic acid-9; paraldehyde-15; amyl alcohol-19; valeric acid-10; toluene-35; aniline-36; nitrobenzene-11; mesitylene-34; turpentine-13; thymol-22; brombenzene-10; picoline-24; pyridine-23, etc.

Correlations of these lines, bands and non-enumerated general absorption areas, with definite structures or "opened-up stages" of the respective molecules are evidently impossible. But the problem is further complicated by a large increase of lines and bands when the substances are studied in the form of vapor.

Hartley,[4] Purvis[5] and others have recently shown that many compounds, studied spectrophotometrically in the form of vapor, give larger general absorption areas, and stronger, wider and more numerous bands, than at ordinary temperatures. Furthermore, varied pressures give similar effects For instance, with piperidine Coblentz[6] finds one band in the infra-red; Hartley[7] and Purvis[8] find no band when it is viewed in an alcohol solution; however, in the form of vapor at 332 mm., Purvis[9] finds *fifteen bands.*

Other results obtained by Purvis, working with compounds at varied temperatures and pressures, are as follows: pyridine[10] (14° and 758 mm.),

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[1] Kayser's "Handbuch der Spectroscopie," Vol. III. See here complex spectra of simple substances. See also Purvis' series of papers, *Proc. Camb. Phil. Soc.*, **14**, 381, 436, 568 (1907); *J. Chem. Soc.*, **95**, 294; **97**, 692, 1035, 1546, 1648; **99**, 2318.

[2] *J. Chem. Soc. Ind.*, **34**, 394 (1915); *Astrophys. J.*, **42**, 4 (1915).

[3] These figures are taken from Kayser's "Handbuch der Spectroscopie," Vol. III. Owing to conflict of authorities, the numbers given cannot be vouched for. However, they are probably more numerous than indicated.

[4] *Phil. Trans.*, **208**, 475.

[5] See references above.

[6] *Astrophys. J.*, **20**, 207.

[7] *J. Chem. Soc.*, **47**, 685.

[8] *Ibid.*, **97**, 712.

[9] *Ibid.*, **97**, 710.

[10] *Ibid.*, **97**, 694.

38 bands; α-picoline[1] (15° and 745 mm.), 14 bands; nicotine[2] and coniine, no bands; quinoline[3] (60° and 865 mm.), one band; aniline[4] (14° and 763 mm.), 83 bands; homologs of aniline, in the form of vapor, no bands; furane[5] (13° and 749 mm.), 15 bands; furfurol[6] (12° and 158 mm.), 21 bands; pyrrol[7] (17° and 760 mm.), 4 bands.

From these and other studies the conclusion is drawn that *absorption bands cannot at present be correlated*[8] *with chemical structures, linkings, dynamic groups, or "opened-up stages."* On the contrary, as was pointed out by Purvis,[9] "a complete explanation of the origin of selective absorption implies a consideration of many and deep-seated factors." Such explanation[10] implies "a balance of a complex series of disturbances, and the forces which determine these include such factors as the number, the mass, the intrinsic characters, and the orientation of the atoms of both the nucleus and the side-chains; the physical conditions of the vibrating system as vapors or in solution or as liquids at various temperatures and pressures: and on the disturbances and reaction of the vibrations consequent on the absorption of the radiant energy by the various oscillating atoms and atomic groups."

Another observation on absorption studies must be made. The ordinary absorption curves, plotted, as they are, from the limits of positions of absorption bands, that is, each band at each observed thickness supplying two points on the coördinate field and all points being linearly connected, must be regarded as *position* curves and cannot properly be interpretated as *dynamic* curves. However, such dynamic interpretations are frequently and erroneously implied or made, yet such interpretations probably are as fallacious as an *object-associated, dynamic* interpretation of a curve derived in a similar manner from the limits of shadows of such object illuminated by an approaching light.

In this connection it must be recalled that the primary assumption in

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[1] *J. Chem Soc.*, 97, 700.

[2] *Ibid.*, 97, 1036. Nicotine shows one band in alcohol solution.

[3] *Ibid.*, 97, 1038; 47, 685. Shows three bands in alcohol solution.

[4] *Ibid.*, 97, 1548.

[5] *Ibid.*, 97, 1648.

[6] *Ibid.*, 97, 1650.

[7] *Ibid.*, 97, 1655.

[8] [In his most recent paper (*Astrophys. J.*, 42, 4 (1915)) and in the reply following, Baly attempts to correlate absorption groups, bands, and lines of the entire spectrum. How well he has done this remains to be seen. However, it must be remembered, as stated above, such correlations may be irrelevant to the phenomena of chemical reactivity. After persuing all of Baly's recent papers, the conviction remains, whereas he has multiplied words and made many dogmatic statements in respect to chemical reactivity, he has thrown no new light on chemical activity and has not, in any one instance, correlated light-vibration phenomena with a definite chemical reactivity.]

[9] *J. Chem. Soc.*, 97, 1659 (1910).

[10] *Ibid.*, 99, 2325 (1911).

correlations of absorption phenomena and chemical constitution, is that similarity of curves indicates similarity of dynamic groups. That this is not true is evident not only in all cases of curves whose ordinates are thicknesses of the same solution[1] but also in studies of the curves themselves.

If comparisons are made of the curves of certain divergently constituted compounds as, for instance, aniline[2] and tetrachloropyridine[3] and acetylacetone[4] and ethyl cinnamate,[5] *p*-aminobenzaldehyde hydrochloride[6] and 4-nitro-*o*-xylene[7] and *p*-nitroanisole,[8] *p*-aminobenzaldehyde[9] and nitrofluorene,[10] etc., it will be observed that their curves are respectively not only nearly identical but that they differ far less widely than the curves of homologs[11] or of the same substance in different solvents. Surely, in the light of our present knowledge, it is hopeless to attempt to correlate absorption phenomena and dynamic groups of so divergent compounds.

Another important observation on absorption spectra studies must be made at this time. Hartley's early experiments were based on studies of different concentrations in equal thickness. Later the method, almost universally employed by Hartley, Baly and others, involved different thicknesses of the same solution. This latter method, while more convenient, brings into the viewed field *static molecules*, hence involves no chemical change other than chemical equilibria. The former method, involving equal thickness of varied concentrations, brings into the viewed field molecules whose number is progressively modified by the solvent,[12] the chemical changes thus resulting being, of course, such as are produced by ionization, hydrolysis, etc. This latter method, therefore, must be more fitted for study of the "opening-up" influence of solvents

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[1] See below.

[2] *J. Chem. Soc.*, 87, 1343.

[3] *Ibid.*, 91, 1124.

[4] *Ibid.*, 85, 1034.

[5] *Ibid.*, 93, 1812.

[6] *Ibid.*, 93, 2110.

[7] *Ibid.*, 97, 574.

[8] *Ibid.*, 89, 518.

[9] *Ibid.*, 93, 2110.

[10] *Ibid.*, 97, 577.

[11] *Ibid.*, 87, 1342–3 (1905); 93, 2110 (1908). Compare benzene and ethyl benzene; aniline, methylaniline and dimethylaniline; *o*-aminobenzaldehyde and *p*-aminobenzaldehyde.

[12] Recently Baly realizes the important influence of concentration on absorption (*J. Chem. Soc.*, 101, 1471 (1912)). "Variation of dilution in any one solvent at once gives an explanation why Beer's law fails to hold in so many cases." Later (*Ibid.*, 103, 91 (1913)), Baly studied acetoacetic ester and pyridine through such a range of concentrations as 10 *N* to 0.0002 *N*, and observed that the "step-out," or limits of transmission of bands, varies progressively but not in accordance with Beer's law.

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,