

CHEMISCH WEEKBLAD

ORGAAN VAN DE NEDERLANDSCHE CHEMISCHE VEREENIGING EN VAN
DE VEREENIGING VAN DE NEDERLANDSCHE CHEMISCHE INDUSTRIE

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INHOUD: Mededeelingen van het Algemeen Bestuur der Nederlandsche Chemische Vereeniging. — Gevraagde en aangeboden betrekkingen. — Prof. W. C. M. Lewis, Some Aspects of Chemical Reactivity. — Boekaankondigingen. — Chemische Kringen. — Personalialia, — Correspondentie, enz.

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SOME ASPECTS OF CHEMICAL REACTIVITY¹⁾

by

W. C. M. LEWIS.

INTRODUCTION.

My subject tonight is a brief, and I fear very inadequate outline of a number of problems in connection with the field of chemical kinetics.

The classical work which laid the foundations of chemical kinetics is essentially that of the van 't Hoff school. Owing to lack of time it is unfortunately necessary to pass over this great work without comment, and I come therefore, without introduction, to the attempt made by Marcelin²⁾ in 1913—14 to deal with the rate of a chemical reaction from the point of view of statistical mechanics. Marcelin's expression is not much use as it stands — it involves an unintegrated integral. What is important about it is that on differentiating with respect to temperature, a surprisingly simple expression — now known as the Marcelin-Rice equation — is obtained which is in complete formal agreement with the equation of Arrhenius, with this difference, however, that a precise statistical meaning is attached to the energy term "E".

The Marcelin-Rice equation is

$$\frac{d \log k}{dT} = \frac{E}{R \cdot T^2} \dots \dots \dots (1)$$

(Actually this is a simplified expression but the correction term is usually negligible).

In this expression, E stands for the amount of energy, (reckoned per gram mole), which a molecule requires, over and above its normal or average energy content, to make it reactive in the chemical sense. The quantity E is consequently called the "critical increment" per gram molecule. This term implies that a molecule in the normal or average state as regards energy content is not reactive and that chemical reaction depends upon the existence of active molecules which constitute in general only a small fraction of the total molecules present. That the fraction of active molecules present is small follows from the relatively large numerical value which we obtain for E; the critical increment being in general large compared with the normal or average energy content.

¹⁾ A lecture delivered at the Universities of Nederland, April-May, 1925.

²⁾ *Compt. rend.* 157, 1419 (1913), *ibid.* 158, 116, 407 (1914). *Ann. phys.* 3, 120—184 (1915).

Perhaps one should not omit to point out that although the Marcellin-Rice equation and that of Arrhenius are formally identical, there is a real difference in the significance of the energy term which raises a theoretical point of some interest. Arrhenius conceived of two distinct forms, two physical isomers of one and the same substance, one form being chemically active and the other chemically inert. The energy term which appears in his equation, as I understand it, is a true heat of activation and indicates the difference between the *average* internal energy of the active form and the *average* internal energy of the inert form. But if we use the term average, we imply that there is a statistical distribution of energy among the molecules of the active form (as well as among the molecules of the inactive form) and that consequently there must be a few molecules of the active form with energy content perhaps no greater than that of the inactive form, which seems almost a contradiction in terms. It may be seriously doubted — as has been done by Tolman³⁾ for example — whether it is legitimate to regard two such forms as thermodynamically distinct. The theoretical basis of the Marcellin-Rice equation does not postulate two such physical isomers; instead it deals with the decomposing substance as a whole and considers the statistical distribution of energy among the various molecules of the substance regarded as a single entity. It would seem that the latter view is likely to be the more correct.

The next stage in the investigation of the mechanism of chemical change is based on the Einstein formulation of the quantum hypothesis, more particularly in the light of the Bohr theory of atomic structure. I here refer to the familiar Einstein Law of photo-chemical equivalence which when viewed in the light of the modified deduction as given by Einstein himself in 1917⁴⁾ is seen to be as applicable to thermal reactions (i. e. ordinary chemical reactions) as it is to photo-chemical reactions. On this basis, we would write the energy term of the Marcellin-Rice equation in the form

$$E = N_0 h \nu \dots \dots \dots (2)$$

where " N_0 " is the Avogadro constant, namely the number of molecules in one gram molecule; " h " is the universal Planck constant and " ν " is the frequency assumed in the first instance to be a single frequency of radiation by the absorption of which a reactant molecule can be activated. This equation represents the quantisation of the statistical result of Marcellin and Rice, but it does not necessarily imply that radiation is the sole or even the main cause of activation of a molecule. Activation may be brought about by collision, for example.

Parenthetically, starting with the idea of critical increment, it will be easily seen that in the case of the equilibrium constant K of a reaction, where $K = k_1/k_2$, the variation of K with temperature is given by

$$\frac{d \log K}{dT} = \frac{E_1 - E_2}{RT^2}$$

and consequently, by comparison with the van 't Hoff isochore, the heat effect = $E_1 - E_2$.

To test equations (1) and (2), the most direct

means would be spectrometrical, i. e., the observation of absorption bands. In fact, if the above equation is applicable to thermal change, i. e., ordinary chemical change, at least one absorption band should be detectable, with its head (presumably) corresponding to the frequency " ν " which ought to be calculable from the value of the energy term E , this in turn being easily calculable from the temperature coefficient of the chemical process under consideration. The question which we have now to consider in some detail is whether this relation is in fact borne out or not in the case of *thermal* reactions. It is necessary to consider gaseous reactions on the one hand and reactions in the liquid state on the other. I wish to begin with the latter.

REACTIONS IN LIQUID SOLUTIONS.

Turning our attention to *uni*-molecular processes, let us first consider the decomposition of triethylsulphonium bromide which has been shown by von Halban⁵⁾ to decompose into ethyl bromide and diethyl sulphide in a unimolecular manner in various solvents. From van Halban's velocity constant data at different temperatures, it is possible by making use of the Marcellin-Rice equation, to calculate the critical increment per grammolecule of the reactant. From this, assuming that one quantum is required per molecule, it is easy to calculate the critical increment per grammolecule of the reactant. From this, assuming that one quantum is required per molecule, it is easy to calculate the frequency of the radiation which would accomplish this degree of activation. The calculated values of the frequency show that the triethylsulphonium bromide should exhibit an absorption band in the short infra red region in the neighbourhood of 1μ , the precise location of the band depending upon the solvent employed. Using an infra-red spectrometer and radiomicrometer, Taylor and Lewis⁶⁾ have observed the absorption spectra of triethylsulphonium bromide in the eight solvents employed by von Halban over the range 0.7μ to 3.6μ . The details of the procedure and measurements are given in the paper cited. It may be remarked that in general the solute is not very soluble, which renders it somewhat difficult in certain cases to determine the band, since this depends upon the difference in transmissive power of the pure solvent and the solution respectively. The results obtained are summarised in the following table.

Decomposition of triethylsulphonium bromide.

Solvent.	Critical Increment E (from von Halban's data) in cal. per mole.	Wavelength of Band Calculated from value of E.	Wavelength Observed.
Nitrobenzene . . .	28390	1.0μ	1.05μ
Tetrachloroethane . . .	31030	0.91	0.90
Propyl alcohol . . .	33960	0.84	0.89
Amyl alcohol . . .	33530	0.85	0.83
Benzyl alcohol . . .	36180	0.78	0.80
Acetic acid . . .	29220	0.97	0.90—0.95
Acetone	{30450 28560}	? 0.96	1.3
Chloroform	? 33320	? 0.85	1.0

³⁾ J. Am. Chem. Soc. 42, 2506 (1920).

⁴⁾ Einstein, Physik. Z. 18, 121 (1917).

⁵⁾ Z. physik. Chem. 67, 129 (1909).

⁶⁾ H. S. Taylor and Lewis, J. Chem. Soc. 121, 665 (1922).

It will be observed that in the first six cases the agreement between the calculated and observed wavelength of the band is satisfactory, thus affording a verification of equation (2). It is important to point out that only a single band was observed over the range examined in each of the above cases. In the case of acetone and chloroform there is serious discrepancy between the observed and calculated positions of the bands. It is significant, however, that it is precisely in these two cases that von Halban observed abnormal behaviour on the part of the velocity "constants", this being attributed by him to the known fact that in acetone the triethylsulphonium bromide is ionised whilst in chloroform it is polymerised. The discrepancy, therefore, cannot be regarded as invalidating the relationship under consideration.

Again in the case of the decomposition of maleic acid in the fused state into fumaric acid (which is almost certainly a unimolecular process) the kinetics of which have been examined by Höjendahl⁷⁾ at temperatures in the neighbourhood of 140° C., the critical increment so obtained is 15800 calories per mole. From this the position of the band is calculated to be 1.8 μ , i. e., in the short infra-red region. Direct measurements of the absorbing power of fused maleic acid have been carried out by Höjendahl who, using three different specimens, has found the head of the band to lie at 1.80 μ , 1.85 μ , and 1.75 μ respectively, in good agreement with the positions calculated. No other band was observed in the region examined, namely from 0.8 μ to 3.5 μ .

We now turn to reactions in liquid solutions which are almost certainly bimolecular. I refer in the first place to the hydrolysis of sugars such as sucrose and maltose in aqueous solution containing hydrogen ion as catalyst. A discussion of the very complicated problem of the mechanism here involved would take too much time. Suffice it to say that one would expect a band in the short infra red, which in the case of maltose ought to lie clear of the water bands themselves. This is shown by the curve given in Figure I.

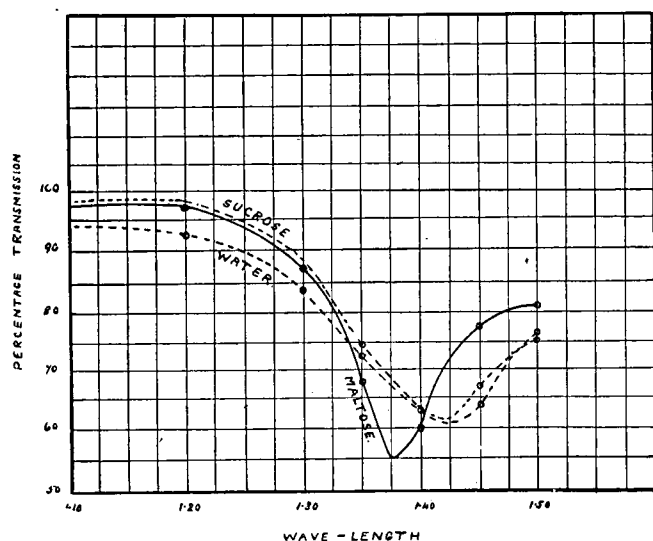


Figure I.

As I have just been referring to the acid hydrolysis of sugars, I would like to add a few words of a

⁷⁾ J. Phys. Chem. 28, 758 (1924).

general nature regarding catalysis in homogeneous solutions.

In the first place it will be realised that in the case of multimolecular chemical reactions occurring in solution there are two ways in which the material environment may affect the rate. This arises from the fact that in general the expression for the speed involves two factors which are multiplied together. The first of these is dependent upon the rate of collision, i. e. upon the number and mobility of the reactant species. The second is an exponential term which contains the critical increment in the form $e^{-E/RT}$. This dimensionless factor is a measure of the fraction of collisions which are chemically effective in so far as at least as energy content is concerned. (It does not allow for orientation considerations). When we alter concentration terms as in the typical H^+ ion catalysis, but keep the same solvent, the E term is relatively unaffected and the alteration in rate is due to the change in the collision term itself, i. e., due to alteration in concentration of reactants reacting stoichiometrically. Although a question of this kind really requires somewhat lengthy discussion, it seems to me that in view of the width of the field, we can best employ our limited time by turning our attention to a few selected cases of chemical change which possess certain characteristic features.

*The Anthracene \rightleftharpoons Dianthracene reaction, photochemical and thermal, and certain inferences that may be drawn therefrom.*⁸⁾

It has long been known that anthracene when dissolved in a solvent such as benzene or phenetol and exposed to light polymerises to dianthracene. The effective wavelengths have been shown to belong to the blue-violet region of the spectrum. Corresponding thereto Dr. Taylor and I have found that anthracene, when dissolved, possesses two well marked absorption bands lying fairly close together at 445 $\mu\mu$ and 475 $\mu\mu$ respectively. For purposes of calculation it will be a sufficiently close approximation to take the mean of these two wavelengths as corresponding to the critical increment of activation of anthracene in order that polymerisation may ensue. That is, the critical increment is 61300 calories. (Incidentally, one may conclude that the known fluorescence of anthracene solution which occurs in the blue region is due to the activated anthracene molecule returning to the normal state and not to dianthracene which is shown by experiment to have no absorption at all in this region of the spectrum). In polymerising to dianthracene, two molecules of anthracene are involved. The point is whether each of them is activated to the same extent or whether one is activated and the other normal. This is best approached by considering the other side, the dianthracene side. It is well known that a solution of dianthracene, say in phenetol, if left in the dark at ordinary temperatures, reverts to anthracene. Luther and Weigert, amongst others, have investigated this reaction at various temperatures and have shown that it is undoubtedly a unimolecular process with a very considerable critical increment amounting to 39300—41000 calories per mole of dianthracene. The mean value is 40000 calories. Further, Weigert

⁸⁾ cf. H. A. Taylor and Lewis, J. Am. Chem. Soc. 46, 1606 (1924).

has shown that dianthracene decomposes into anthracene with an evolution of heat amounting to 20000 calories (in round numbers) per mole of dianthracene. Applying the relation already referred to connecting critical increments with heat of reaction it follows that the total critical increment of *polymerisation* reckoned for two moles of anthracene is 60000 calories. This is so close to the value 61300 calories as to leave us in no doubt but that in the case of the polymerisation, the photochemical observation and the locating of the absorption band have led to a reasonably correct value of the activation necessary. The simplest conclusion is that the polymerisation process involves essentially the activation of one molecule of anthracene to the high degree represented by 60000 calories per mole and that this molecule then combines with a normal unactivated molecule to give the polymer. This is a somewhat surprising result. On general grounds, one would have expected activation of both molecules and since they are quite similar, one would have expected equal activation of both. If this were so, anthracene should show an absorption band at a wavelength in the region of $920 \mu\mu$, which it does not show, and photo-polymerisation should be brought about by exposure to light of this wavelength, which is also contrary to fact. Investigation of the absorption spectrum of anthracene over the short infra-red range from 0.8μ to 3.8μ disclosed the presence of only one band with its head at 1.8μ .

It follows from the above statement of the behaviour of anthracene and dianthracene that the latter, the dianthracene, should exhibit absorption and should be photochemically *depolymerised* at a wavelength region corresponding to the critical increment term 40000 calories, that is at a wavelength of $707 \mu\mu$. We looked for absorption here but owing to the slight solubility of dianthracene (as compared with anthracene) no band was detected under the conditions of

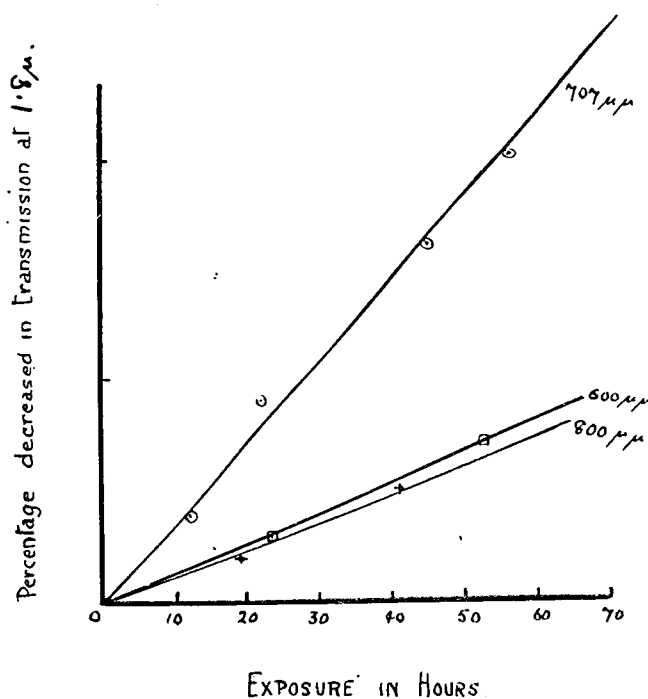


Figure II.

measurement. What we have been able to do, however, is to bring about for the first time the *photo-de-*

polymerisation of dianthracene (as distinct from the long familiar thermal depolymerisation) by exposing a solution to light of wave length $707 \mu\mu$. The accompanying figure, Fig. II, shows that the region $707 \mu\mu$ is in fact responsible for the change, and this confirms to a considerable extent the view I have just put forward. I may add that, so far as our measurements could tell us, dianthracene is a very transparent substance; it shows no detectable bands in the short infra red region or in the visible. In the ultra violet region the bands it shows are identical with those of anthracene. It would be of great interest to know by X-ray methods whether the crystalline form of dianthracene differs from that of anthracene. No information is available.

I have already pointed out that the most striking conclusion which we have drawn from the behaviour of anthracene in respect of its polymerisation is that, of the two reacting molecules, one is highly activated, the other not at all. One naturally enquires whether this may be a general feature of all bimolecular processes. It would be premature at this stage to dogmatise, as too few cases have been investigated. I would like, however, to mention that this conclusion appears to be borne out by quite a different reaction, namely that involving the activation of sulphur vapour, cf. Norrish and Rideal⁹⁾. This happens to be a gaseous reaction but I am considering it here for the moment only. I shall take up gaseous reactions by themselves later. The reaction considered is the union of hydrogen and sulphur vapour to form hydrogen sulphide. The critical increment of this amounts to 50000 calories reckoned per atom of sulphur, or 100000 calories per mole of sulphur, for sulphur vapour at a fairly high temperature consists largely of S_2 molecules. Now the characteristic absorption band of sulphur vapour at fairly high temperatures occurs at $275 \mu\mu$ ¹⁰⁾ which corresponds to 103000 calories. The inference to be drawn here is, I think, that in the union of sulphur and hydrogen, the hydrogen does not require any sensible activation but that the sulphur molecule requires a very high degree of activation.

ADDITION REACTIONS:
ORGANIC BASE + ALKYL HALIDE.

The question of activation of a single component in order to make a bimolecular process occur may be considered in relation to a type of reaction which occurs in the liquid state and which we would have expected to be of a very simple kind. The reaction I have in mind is that of addition of an alkyl halide to a substituted amine to form the addition salt-like compound. Let us take the case of ethyl iodide and a number of aromatic bases as examined by Hirniak¹¹⁾ in *methyl* alcohol solution. On calculating the critical increment from Hirniak's velocity constant data, one obtains the following: —

⁹⁾ J. Chem. Soc. 125, 2079 (1924).

¹⁰⁾ Exposure of H_2 and S_2 vapour to this region of the spectrum has been shown by Rideal and Norrish to cause photochemical union of the two gases.

¹¹⁾ Tables Ann. II, 503 (1911).

Base	E	Base	E
Dimethyl-p-toluidine	16.700	β Naphthoquinoline	24.200
Pyridine	19.200	α Picoline	21.900
Quinoline	23.000	Collidine	24.400
Isoquinoline	19.000	α Naphthoquinoline	25.200

It will be observed that E varies with the nature of the base. An analogous variation has been observed for other bases reacting with ethyl iodide in solvents other than methyl alcohol. I might refer in this connection to the very accurate unpublished data obtained by Mr. T. Byrne whose values of E are given in the next table.

Base.	Solvent.	k_{vi} .	E.
Thio-urea	ethyl alcohol	1.06×10^{-4} (25° C.)	14700
"	acetone	3.14×10^{-4} "	13700
Thio-carbanilide	acetone	3.2×10^{-5} "	15700
Quinoline	ethyl alcohol	1.69×10^{-7} "	28200
Dimethylaniline	ethyl alcohol	8.50×10^{-6} (45° C.)	20700
"	acetone	1.17×10^{-5} "	13700
Pyridine	ethyl alcohol	7.89×10^{-6} "	20600

On the other hand, if we examine the extensive results of Segaller¹²⁾ for the reaction between sodium phenoxide and a whole series of alkyl iodides in the solvent ethyl alcohol, we find a constant value for the critical increment namely 20600 calories. This is shown in the following table: —

Iodide	E	Iodide	E
Methyl Iodide	20.900	Isobutyl Iodide	20.300
Ethyl "	21.000	Isoamyl "	20.900
Propyl "	21.500	Isopropyl "	20.400
Butyl "	20.500	Secondary Butyl Iodide	20.800
Amyl "	20.600	" Amyl "	20.900
Hexyl "	20.600	" Hexyl "	20.600
Heptyl "	20.800	" Heptyl "	20.500
Octyl "	21.100	" Octyl "	20.600
Hexadecyl "	21.300	Tertiary Butyl "	21.600

In the above case it is logical to conclude that the iodide does not require activation since it is very unlikely that the degree of activation would be the same for, let us say, methyl-iodide and hexadecyl iodide. If we can assume that this is likewise the case in the Hirniak and the Byrne experiments it would follow that the observed critical increments which varied from base to base are to be ascribed to the individual bases.

With this conclusion in mind, Byrne determined with great care the infra red absorption spectra of a mixture of thio-urea and the iodide in ethyl alcohol and also dimethyl anilin and the iodide in alcohol. He also examined the solution of the resulting addition compound. In all these cases precisely the same type of absorption manifested itself namely a broad, deep band in the region of 3μ . Now it is well known that organic bodies containing the OH group exhibit this band. It is also known that the NH_2 group is characterised by a band almost at the same position, namely 2.98μ . We must infer therefore from the absorption spectra in the infra red that neither the

base nor the resulting addition compound exhibits a band characteristic of a critical increment say of the order 15000 to 20000 calories. So far as absorption spectra go, we are only justified in inferring that the base is being activated at its ordinary position, namely 2.98μ , and consequently that the critical increment in the cases examined by Hirniak and by Byrne ought to be about 9800 calories. But the observed critical increments are greater than this, in some cases very much greater. The discrepancy is itself variable from base to base and is far beyond what can be attributed to the iodide. An examination of a variety of reactions of this type suggests, I think, that we are not dealing with a simple addition reaction of alkyl halide to the electrically neutral, molecular form of the organic base, but that the measured reaction is preceded by a rapidly attained equilibrium probably identical with, or very similar to, ionisation of the base and that it is the basic cation which is essentially involved. If this be so, it is obvious that the heat of ionisation or an analogous term characteristic of each organic base ought to play a significant role in the magnitude of the critical increment observed for the so-called addition reaction. This aspect has not been worked out as yet. In a few cases only are the heats of ionisation of organic bases known and these only for aqueous solutions. There are no data for organic solvents. By analogy with the values for aqueous solutions we might say, however, that the heats of ionisation of the bases in organic solvents would vary from 5000 to 10000 calories, which would lead to values of the correct order of magnitude for the true critical increment of reactions of the type considered. In fact we now expect on this basis that

$$E_{\text{observed}} = E_{\text{true}} + Q$$

where E_{true} is not far from 9800 calories and Q is the heat absorbed in the ionisation (or other preliminary activation) of the base. I would like to remark that if the reaction between alkyl halide and organic base is of the kind suggested one would expect that the speed of the reaction should be accelerated by the polar nature of the solvent, by a trace of water, or by such solutions as NaOH and Sodium ethylate. Whether this occurs or not I do not know. I may, however, recall that, following quite a different line of reasoning, F. O. Rice¹³⁾ has inferred that this type of reaction may be catalysed by OH-ion. What I wish really to emphasise, however, is that in such cases the position of the infra red absorption band may be employed to give a hint as to a mechanism or at any rate to point to the necessity for new data.

Reviewing reactions in liquid solutions in so far as we have yet gone, I think it may be said that on the whole the simple requirements connecting the position of a band with the magnitude of the critical increment are satisfied. It is a very different story when we come to consider gaseous reactions.

Before going on with gaseous reactions, however, I would like to take up as briefly as possible the problem presented by the ionisation of a dissolved electrolyte, the electrolyte being one whose ionisation obeys the law of mass action as ordinarily applied. The problem we are concerned with is the magnitude of the energy terms involved in ionising the molecule

¹²⁾ J. Chem. Soc. 105, 106 (1914).

¹³⁾ J. Am. Chem. Soc. 46, 2416 (1924).

and involved in the recombination of the ions; and we have to consider how such energy terms vary with the nature of the solvent, that is, the effect of material environment upon the ionisation process.

INFLUENCE OF ENVIRONMENT ON THE IONISATION OF A DISSOLVED ELECTROLYTE.

About 20 years ago, Godlewski¹⁴⁾ published some measurements on the degree of ionisation of moderately strong electrolytes, namely salicylic, cyanacetic and bromoacetic acids, in mixtures of alcohol and water. The most striking result was the truly enormous influence exerted upon the degree of ionisation on passing from a completely aqueous to a completely alcoholic solution. A few years ago, one of my students, Neale¹⁵⁾, found something similar for the ionisation of picric acid in acetone-water mixtures, and Pring last year¹⁶⁾ found a similar behaviour for weak bases in acetone-water mixtures. Quite recently, one of my students, F. Bradley, has revised Godlewski's work and carried it a good deal further. I propose to consider the main points which Bradley has dealt with.

In attempting to allow for the nature of the solvent on such a problem as ionisation, we naturally turn to the dielectric constant, and indeed, several attempts in this direction have been made, without much success however.

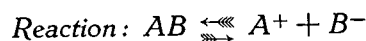
Before any theoretical considerations can be applied, it is essential to have accurate ionisation data. I think I can say that Bradley has obtained data of a much greater accuracy than that of Godlewski for the two acids, salicylic and cyanacetic. The first step is the obtaining of the value of the equivalent conductivity at infinite dilution. Bradley found that the most exact method was to employ the independent mobility of ions. The resulting ionisation constants at the two temperatures 25° and 35° are given in the next table.

per cent alcohol	$K \times 10^5$ ¹⁷⁾ Salicylic Acid		$K \times 10^5$ Cyanacetic Acid	
	25°	35°	25°	35°
0.0	100.0	103.0	320.0	304.0
16.2	66.0	65.3	190.0	180.0
33.2	26.0	25.0	94.0	88.0
52.0	9.0	8.8	36.0	33.9
73.5	1.8	1.7	8.4	7.4
85.7	0.45	0.40	1.7	1.4
89.0	0.25	0.23	1.0	0.9
93.3	0.08	0.07	0.37	0.33
97.8	0.01	0.01	0.05	0.045
100.0	0.00024	0.00026	0.0032	0.0030

It will be observed that on passing from water as solvent to alcohol as solvent the ionisation constant falls to less than one hundred thousandth of its value in water. It is this enormous magnitude which is the characteristic feature of the behaviour and it is this which constitutes the essential difficulty of the problem, namely how to account for it on as simple a basis as possible.

The fundamental idea with which Bradley starts is that the energy terms involved in ionisation depend upon the dielectric constant of the surrounding me-

dium. This is equivalent to saying that in ionisation we are dealing with electrostatic forces of attraction. On this basis the simplest formulation of the process is summarised as follows: —



$$\text{Rate of ionisation} = k_1 e^{-E/RT} \times C_{AB}$$

$$\text{Also } E = E_0/D$$

$$\text{Rate of combination of ions} = k_2 e^{-E'/RT} \times C_{A^+} \times C_{B^-}$$

$$\text{Also } E' = E'_0/D$$

Equilibrium condition: —

$$\frac{C_{A^+} \times C_{B^-}}{C_{AB}} = K_{\text{obs}} = \frac{k_1}{k_2} e^{(E'_0 - E_0)/DRT} \quad (1)$$

The E' term denotes the work necessary to remove the solvent molecules with which the ions become hydrated. On the basis of equation (1) just given, we have now to see how far the considerations employed may be applied to the observed ionisation constants. To obtain the values of the constants k_1/k_2 and $E'_0 - E_0$ in equation (1), two of the observed ionisation constants are substituted and the equation solved. In the case given in the next table, the values thus used are shown in brackets in the last column but one.

Salicylic acid, 25°.

per cent alcohol	dielectric constant	$K_{\text{obs}} \times 10^5$	$K_{\text{calc}} \times 10^5$ (Equation 1)	$K_{\text{calc}} \times 10^5$ ($K_2 D^3$)
0.0	78.5	100.0	(100.0)	(100.0)
16.2	66.5	66.0	55.2	60.8
33.2	55.9	26.0	26.4	36.1
52.0	45.5	9.0	9.2	19.5
73.5	35.0	1.8	1.7	8.9
85.7	29.7	0.45	(0.45)	5.4
89.0	28.3	0.25	0.29	4.7
93.3	27.0	0.08	0.19	4.1
97.8	25.3	0.01	0.09	3.3
100.0	24.9	0.0002	0.08	3.2

The value of $E'_0 - E_0$ works out at -153700 calories. That this would be expected to be negative is fairly evident since the energy required to ionise a molecule must be considerably greater than the energy required to dehydrate an ion and it is to be remembered that E_0 and E'_0 refer to a hypothetical medium of dielectrical constant unity where energy terms of this kind must be exceedingly large. (You will recall the data of Fajans and others in a similar connection).

If you examine the above table, you will note on comparing the columns headed (K_{observed}) and ($K_{\text{calculated}}$ by equation (1)) that the agreement is quite good for water as solvent up to 90 % of alcohol, which represents a very considerable range in composition of solvent, but that beyond this region the discrepancy is so serious — in the sense that the actual ionisation is decreasing with increasing alcohol content much more rapidly than that calculated — the discrepancy is so serious that we are forced to conclude that the simple, mainly physical, considerations underlying equation (1) are inadequate. For this reason, Bradley introduces what he calls chemical considerations in which a more definite part is attributed to the solvent. Bradley finds, as indeed one would expect, that these chemical considerations prove to be only of first importance, so far as numerical values are concerned, over the range of alcohol-water

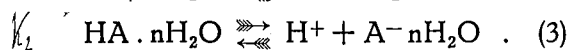
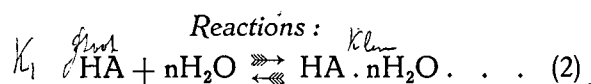
¹⁴⁾ J. chim. phys. 3, 393 (1905).

¹⁵⁾ Trans. Faraday Soc. 17, 505 (1921).

¹⁶⁾ Ibid. 19, 705 (1924).

¹⁷⁾ rounded values, measured at a dilution of 1024 litres.

mixtures containing very little water, the values already calculated over the remaining range being comparatively little affected. The more detailed considerations regarding the mechanism involved are outlined in the next paragraph.



$$K_{obs} = \frac{[H^+][A^- \cdot nH_2O]}{[HA]} = K_1 K_2 [H_2O]^n$$

where $K_1 = \frac{[HA \cdot nH_2O]}{[HA][H_2O]^n}$, and $K_2 = \frac{[H^+][A^- \cdot nH_2O]}{[HA \cdot nH_2O]}$

Also $K_2 = \frac{k_1}{k_2} e^{(E'_0 - E_0)/DRT}$

$$\therefore K_{obs} = K_1 \left(\frac{k_1}{k_2}\right) [H_2O]^n e^{(E'_0 - E_0)/DRT} \quad (5)$$

But $n = 2$

$$\therefore K_{obs} = K_1 \left(\frac{k_1}{k_2}\right) [H_2O]^2 e^{(E'_0 - E_0)/DRT}$$

$(E'_0 - E_0$ for Salicylic Acid = -113900 cal. p. mole.
 „ „ Cyanacetic Acid = -112600 „ „ „

(Parenthetically I would point out that n , the number of molecules of monohydrate with which one molecule of the unionised acid becomes hydrated, can be easily obtained by applying equation (5) to a limited range where the amount of water is small. It is thence found that $n = 2$).

In equations (2), (3) and (4), we are allowing for hydration of the unionised molecule as well as of the ions, it being assumed that it is the hydrated form which really ionises and at the same time it is assumed that the concentration of the hydrated unionised molecule is small compared with that of the unhydrated unionised molecule. There is undoubtedly a considerable degree of arbitrariness about such an assumption but the results obtained seem to confirm it as is shown by the next two tables.

Salicylic Acid, 25°.

per cent alcohol	Dielectric constant	Activity of water	$K_{obs} \times 10^5$	$K \text{ calc.} \times 10^5$
0.0	78.5	23.7	100.0	(100.0)
16.2	66.5	21.4	66.0	56.0
33.2	55.9	19.5	26.0	27.0
52.0	45.5	18.1	9.0	10.7
73.5	35.0	15.5	1.8	2.2
85.7	29.7	12.0	0.45	(0.50)
89.0	28.3	10.1	0.25*	0.26
93.3	27.0	7.0	0.08*	0.09
95.0	26.0	5.3	0.04	0.04
97.8	25.3	2.5	0.01*	0.007

The observed ionisation constants marked * are due to Goldschmidt¹⁸).

Cyanacetic Acid, 25°

per cent alcohol	Dielectric constant	Activity of water	$K_{obs} \times 10^5$	$K \text{ calc.} \times 10^5$
0.0	78.5	23.7	391 to 318	(362)
16.2	66.5	21.4	231 to 188	191
33.2	55.9	19.5	116 to 94	92.5
52.0	45.5	18.1	46 to 36	36.8
73.5	35.0	15.5	9.5 to 8.4	7.8
85.7	29.7	12.0	1.8 to 1.7	1.8
91.0	27.3	8.8	0.73	0.55
92.7	26.8	7.7	0.45	0.36
94.4	26.3	6.5	0.26	0.22
95.0	26.0	5.3	0.14	(0.14)
96.2	25.8	4.8	0.12	0.11
98.1	25.4	3.0	0.05	0.04

On examining the data of the above tables, it will be seen that we have now succeeded in obtaining a very satisfactory degree of agreement between observed and calculated ionisation constants over a wide range extending from zero to 98 % alcohol. Naturally, from the form of equation (5) (which contains the activity of water) it is impossible to apply it to 100 % alcohol. There are of course a number of subsidiary considerations which enter more particularly into the region 95 % to 100 % alcohol, such as the competition of alcohol and water for the ions, but these I do not propose to deal with. I am concerned rather with the general nature of the problem. In this connection I would draw attention to the values obtained for the quantity $E'_0 - E_0$. In the case of salicylic acid this is -113900 calories and in the case of cyanacetic -112600. If we take it that E'_0 is negligibly small compared with E_0 (as would be inferred from the chemical stability of the undissociated molecule and chemical instability of a hydrated ion) it would follow that E_0 is of the order 100000 calories. Now to conceive of ionisation of a molecule in the gaseous state (which is in effect what E_0 refers to) it is clear that a very large value, fully 100000 calories, would be anticipated. Ionisation potentials in gases indicate values greater than this. Similar large values would be expected from the heat of ionisation as ordinarily calculated on crystal lattice theory. It is to be remembered, of course, that the actual critical increment of ionisation is E_0/D where D is the dielectric constant. Hence, for water as solvent, the actual critical increment is of the order 1000 to 2000 calories, a value which is in agreement with the fact that the rate of ionisation is immeasurably fast.

There is a point in connection with this problem of ionisation which I would like to mention. If the critical increment of ionisation really depends on the dielectric capacity of the system as we have been supposing is the case, then the electro-valent bond necessarily concerned must be of the electrostatic kind, that is the unionised molecule is polarised. A sharp distinction would therefore have to be drawn between electrovalency and covalency, since in the latter case, (represented say by the figure-of-8 orbits of a diatomic gas molecule) there is no reason for introducing dielectric constant. The behaviour of triethylsulphonium bromide is a good illustration of the two kinds of linkages. In organic solvents (especially solvents of low dielectric constant) this salt decomposes into diethylsulphide and ethylbromide. In a solvent of high dielectric constant, such as water, this decompo-

¹⁸) Z. physik. Chem. 91, 46 (1916).

sition does not take place; instead the salt ionises into bromide ion and triethylsophonium cation.

Let us return to the actual case of salicylic and cyanacetic acids and consider the equilibrium as represented by equation (5). If this expression is sufficiently accurate and true, it should of course permii us to calculate the ordinary thermodynamic heat of ionisation of such an electrolyte. The steps involved are given in the following equations.

HEAT OF IONISATION.

$$\frac{d \log K_{\text{obs}}}{dT} = \frac{d \log K_1}{dT} + \frac{d \log k_1/k_2}{dT} + \frac{2d \log [H_2O]}{dT} + \frac{d(E'_o - E_o)}{dT} \cdot \frac{1}{DRT} \quad (6)$$

$$\frac{d \log K_{\text{obs}}}{dT} = \frac{d \log K_1}{dT} + \frac{d(E'_o - E_o)}{dT} \cdot \frac{1}{DRT} \quad (7)$$

$$\therefore Q = RT_2 \frac{d \log K_1}{dT} - \frac{(E'_o - E_o)}{D} - \frac{T(E'_o - E_o)}{D} \cdot \frac{d \log D}{dT} \quad (8)$$

$$Q = Q_1 - \frac{(E'_o - E_o)}{D} - \frac{T(E'_o - E_o)}{D} \cdot \frac{d \log D}{dT} \quad (9)$$

$$Q = 1300 - \frac{(E'_o - E_o)}{D} - \frac{T(E'_o - E_o)}{D} \cdot \frac{d \log D}{dT} \quad (10)$$

In the above table, Q is the nett thermodynamic heat of ionisation and Q_1 is the heat of hydration of the undissociated molecule of the acid.

Q_1 can be evaluated by taking the case in which there is no alcohol present. In this way, Bradley finds $Q_1 = 1300$ calories. We consequently arrive at equation (10). On examining the numerical values of each term on the right hand side of equation (10) it is found that the predominant one is the last one, namely

$$\frac{T(E'_o - E_o)}{D} \cdot \frac{d \log D}{dT}$$

Owing to this, it would follow from equation (10) that the nett heat effect should always be heat evolved (denoted by negative sign) for alcohol-water mixtures as solvent. This is by no means the case as is shown by the next table.

Heat of ionisation of salicylic acid at 30°.

per cent alcohol	Observed heat	Calculated heat.
0.0	+ 500 cal.	(+ 500) cal.
16.2	- 200	+ 200
33.2	- 300	- 200
53.0	- 400	- 900
73.5	-1200	-2100
85.7	-2200	-3100
95.0	-1700	-4000
100.0	+ 800	-4300

It will be seen that the equation holds for a range but fails when we arrive at a high alcohol content. One must infer that equation (5) upon which equation (10) is based, although partly true, is nevertheless incomplete. It represents, however, the stage to which this problem has been brought. It is perhaps right to point out that salicylic and cyanacetic are very unsuitable acids wherewith to test equation (10) (as distinct from equation (5)) owing to the very small

nett heat of ionisation Q which is got, by the way, from the observed ionisation constants at two temperatures rather too close together. What one wants is an electrolyte similar to the two acids mentioned, but characterised by a really marked nett heat of ionisation. Up to now, I have not been able to discover a suitable one.

REACTIONS IN HOMOGENEOUS GASEOUS SYSTEMS.

When dealing with liquid solutions so far as data are at present available, I have already said that on the whole the simple requirement connecting the position of the head of the band with the magnitude of the critical increment of the chemical process is satisfied. I added, however, that it is a very different story when we come to consider gaseous reactions.

One of the main difficulties in connection with gaseous reaction is an experimental one, namely the difficulty of being certain that the reaction considered is really occurring in the homogeneous gaseous phase and is not occurring sensibly at the walls of the containing vessel. It is not always an easy matter to tell, and special precautions have to be taken to distinguish between the two modes of occurrence. It has been shown in recent years that several reactions which had hitherto been regarded as true homogeneous ones are in fact principally surface catalysed processes and are consequently wholly unsuitable for the point we have more immediately in view. It is very necessary, therefore, to proceed with extreme caution and it thus turns out that the true gaseous reactions so far investigated are very few in number.

But when we have thus proceeded to eliminate the doubtful cases and have fixed our attention on those about which we are at least moderately certain that they occur as homogeneous processes, (at least over certain temperature ranges) we are forced to the very remarkable and decidedly disturbing conclusion that *in general* the critical increment does *not* correspond to an absorption band.

Let us consider in the first place the *thermal* decomposition of ozone. Ozone is known to be decomposed thermally in a *bi*-molecular manner and at a measurable rate at temperatures of the order of 100°-C. Assuming the existence of activated forms and substituting the observed velocity in the expression for the rate of a bimolecular reaction as given on the basis of simple kinetic theory considerations¹⁹⁾ namely

$$\text{rate} = 2\sqrt{2} \cdot \pi \sigma^2 N^2 \cdot \bar{u} \cdot e^{-E/RT}$$

where N is the number of molecules per cc., \bar{u} the root mean square velocity of translation of the molecules and σ the range of approach of two molecules at a collision, one can calculate the exponential term for the two moles of ozone reacting. It is thus calculated that $E = 23600$ calories. This value depends to a large extent upon the accuracy of the value chosen for σ , the range of approach in a collision between two ozone molecules. This value of E agrees satisfactorily enough with the experimentally determined value namely 26000 obtained by Clement²⁰⁾. I must mention incidentally at this point that

¹⁹⁾ Lewis, J. Chem. Soc. 113, 471 (1918).

²⁰⁾ Clement, Ann. Phys. [4] 14, 342 (1904).

an alternative equation (leading to E values a few thousand calories larger than those required by the above equation) will have to be considered later. The numerical difference is not of great importance for the purpose I have immediately in view, namely the location of the absorption band.

E represents the amount of energy which must be supplied in order to enable two gram-molecules of ozone to react together. Whether it is correct to divide the energy term in half and ascribe E/2 to each gram molecule is uncertain, especially in view of the result referred to in the case of anthracene polymerisation. It is evident, however, that we may regard the quantity 23600 calories or 11800 calories as characteristic of a low partial activation of the ozone molecule. The absorption band to be anticipated would be 1.20μ or 2.40μ both values lying in the short infra red region. So far as investigation has gone, no band has as yet been observed at either position though it is only fair to point out that measurements in the region of 1μ are exceedingly difficult. It is worthy of note, however, that according to Warburg and Leithauser²¹⁾ ozone possesses a characteristic absorption band at 4.756μ which is practically half the frequency of the possible band 2.40μ or one fourth that of 1.20μ band; and multiple relations have been shown by Baly to be not infrequently met with in absorption spectra.

It is only right to add in this particular case, however, that the region around 1μ has not been as yet examined with care — the matter is about to be undertaken in my laboratory — and until this is done it must be left a somewhat doubtful question whether ozone shows a discrepancy or not from the simple relationship.

In addition to the bimolecular decomposition of ozone, reference may also be made to three other bimolecular reactions the kinetics of which have been examined with some care. These are the decomposition of hydrogen iodide by Bodenstein and of nitrous oxide and chlorine by Hinshelwood and his co-workers²²⁾. The velocity constants in these three cases have been determined at more than one temperature from which the corresponding critical increment can be calculated. The values are: —

Gas.	E for two moles.
Nitrous oxide	58500 calories.
Hydrogen iodide	44000 "
Chlorine monoxide	21000 "

We have now to look at these results from the point of view of absorption spectra. In the case of nitrous oxide and hydrogen iodide the values of E would lead us to expect a band about the middle of the visible spectrum. It is well known, however, that these gases are colourless. The value of 22000 calories for chlorine monoxide would lead us to expect a band in the very short infra red. No measurements have been carried out and the position in this case is similar to that of ozone.

It must be pointed out that in what I have just been saying about the lack of agreement between calculated and observed position of band I have been

assuming that only one molecule has to be activated in these bimolecular processes. It might be argued, of course, that this is not generally true and that in gases activation of both molecules in a bimolecular process is necessary. Now in the type of reaction we have been considering the two molecules are chemically similar and consequently if each has to be activated it is reasonable to expect an equal degree of activation. This would mean that the positions of absorption should be sought at regions corresponding to just one half the energy values quoted above. In brief, the short infra red region is indicated. At the present time there are no data available and we cannot go further in this direction until the necessary measurements have been made.

Now let us take the case of a bimolecular gaseous reaction between dissimilar molecules, say, hydrogen and iodine. The total critical increment of this reaction is 40000 calories, an energy term which would correspond to the middle of the visible region of the spectrum. Now hydrogen is absolutely transparent throughout the visible whilst iodine vapour absorbs there, though the head of the band corresponds not to 40000 calories but to about 56000 calories. It would seem, however, that the observed critical increment is associated with the iodine and not with the hydrogen, a conclusion which suggests a relatively high activation of one molecule rather than a low activation of both constituents in the case of gaseous reactions also. In the same connection it is necessary to recall the case of hydrogen and sulphur vapour already mentioned incidentally in which the observed critical increment (100000 calories) agrees almost exactly with the so-called head of the S_2 band according to Rideal and Norrish, the wavelength of which corresponds to 103000 calories. This likewise suggests activation of one constituent, but it is as disconcerting to find in this solitary instance apparent agreement between position of band and magnitude of critical increment as it is to find apparent disagreement in all other bimolecular gaseous cases so far known. I must emphasise once again, however, that when the necessary measurements have been made in the short infra red region the position so far as bimolecular reactions are concerned may be more satisfactory.

Turning from bimolecular processes to unimolecular gaseous reactions we are disappointed to find that there is at best but a single case yet known, namely the decomposition of nitrogen pentoxide, which is really homogeneous, although even in this case, homogeneous catalytic effects are not as yet entirely excluded. The critical increment of this reaction is known to be 24700 calories which corresponds to the very short infra red, at which region, according to Daniels, no absorption manifests itself.

As regards the absence of a band at the expected position, I would like to draw attention to a suggestion made by Franck²²⁾ namely that an absorption band will only manifest itself when in addition to the quantum jump of the electrons the absorbing molecule as a whole is at the same time set into vibration by the reversal of the electron quantum jump. (I take it that Franck's idea means vibration of the nuclei). On this basis, Franck explains sensitisation by addition of foreign material and the strong fluorescence of bodies at low temperature, the fluorescence indicating, so to

²¹⁾ Warburg and Leithauser, Ann. Phys. [4] 28, 313 (1909).

²²⁾ cf. J. Chem. Soc. 125, 1841 (1924).

speak, absorption which failed to take place permanently owing to the immobility of the atomic or molecular structures as a whole.

ON THE MECHANISM OF CHEMICAL CHANGE.

Having reviewed the problems presented by the critical increment and the spectroscopic location of absorption bands, we have now to pass to the further problem of the attempts which have been made to account for the observed velocity of chemical processes.

In the case of bimolecular gaseous processes, adopting the concept of collisions between activated molecules the appropriate expression (1) (given below) appears to fit the facts at any rate approximately.

The expression referred to for chemically similar molecules is:

$$\text{rate} = 2 \sqrt{2} \cdot \pi \cdot \sigma^2 \cdot u \cdot N^2 e^{-E/RT} \quad (1)$$

where σ is the range of approach of two molecules at a collision, u the root mean square velocity, N the number of molecules per cc, and E is the total critical increment. This equation has been shown to apply moderately well to the bimolecular decomposition of ozone.

In the case of nitrous oxide, hydrogen iodide and chlorine monoxide, the degree of applicability of equation (1) is shown in the following table.

Bimolecular decomposition of	E_1 in calories	E_2 in calories	T absolute
Nitrous oxide . . .	55000	58500	956
Hydrogen iodide . .	43600	44000	760
Chlorine monoxide .	22000	21000	384

E_1 = critical increment from velocity equation. (1)

E_2 = " " " observed temperature coefficient.

In the calculations, σ is set equal to 4×10^{-8} cm.

Hinshelwood (to whom the above table is due) remarks that "the fact that the heats of activation [critical increments] for the three reactions run parallel with the temperatures at which the respective velocity constants have the same value (0.0914 moles per litre per second) would seem to dispose effectively of the objection that the agreement may be accidental". It is only right to point out, however, that the agreement obtained depends on the value 4×10^{-8} chosen for σ . If a smaller value were taken, the resulting E value would also be smaller.

The above expression presupposes the existence of activated molecules. It does not in itself give us any guide as to how the activation is brought about. The fact that it applies seems, however, to constitute evidence for the real existence of activated forms. By activated form I mean a molecule whose structure, through displacement of internal parts, differs physically from one with normal energy content. It is only right for me to point out, however, that Hinshelwood and his coworkers²³⁾ employ the above equation but regard the term E simply as that energy value which must be attained by the sum of the translational kinetic energies due to relative speed of approach of

²³⁾ Z. Physik 9, 259 (1922).

²⁴⁾ cf. for example, J. Chem. Soc. 125, 1842 (1924).

the two colliding molecules. When the joint kinetic energy of relative motion attains or exceeds E , chemical change takes place. On this basis the concept of an activated state is really no longer used. It is certain, however, that the formulation of this collision hypothesis will not be given by equation (1) but by the following expression:—

rate of combination = twice the collision frequency

$$= 2 \sqrt{\pi} \cdot N^2 \cdot \sigma^2 \cdot u_c \left(\frac{E}{RT} \right)^{1/2} e^{-E/RT} \quad (2)^*$$

where σ and N have the same significance as before, u_c is the critical speed of relative motion of approach and $E = \frac{1}{4} M u_c^2$, where M is the grammolecular weight. The above expression is sensibly identical with that given by Franck²⁴⁾.

The applicability of equations (1) and (2) above may be tested by calculating by their aid the respective values which have to be ascribed to the energy term E in order to account for the observed velocity of reaction at a given temperature and then to compare the energy term thus obtained with what may be called the observed value, namely the critical increment obtained from the experimental velocity constants at two different temperatures.

On carrying out such calculations and setting as before $\sigma = 4 \times 10^{-8}$ cm., we find that the E values given by equation (2) are apparently about 3000 calories greater than the observed. A discrepancy of this order may be removed, however, by diminishing the value of σ , which still retains possible magnitudes about 1×10^{-8} cm. In fact, if equation (2) is the proper one to apply, it follows that transfer of energy only takes place when the two colliding molecules have so to speak interpenetrated one another somewhat.

At the present time, therefore, owing to the uncertainty regarding σ and to a less extent to the inevitable error in the experimentally determined values of the critical increment it is impossible to distinguish with certainty between equations (1) and (2). That is we are unfortunately unable to settle whether, in the case of bimolecular reactions in gases, activated forms really exist. I may mention, however, that in the case of unimolecular reactions activated forms with an exceedingly brief life period are generally assumed to exist. If they do not exist, obviously any collision hypothesis of unimolecular change is at once ruled out.

It may be well to emphasise perhaps that if equation (1) should turn out eventually to be the truly applicable expression this of itself would not decide how the initial activation was brought about. What would be implied would be that the rate of activation is greater than, and probably much greater than, the rate of bimolecular chemical combination.

In connection with the problem of comparing equations (1) and (2) one is naturally led to inquire whether the value required by equation (1) regarding the average duration of a molecule in the activated state is compatible with estimates formed on other grounds. Without going into any detail I may say

*) Alternatively, equation (2) may be written:

$$\text{rate} = 4 \sqrt{\frac{\pi}{3}} \cdot N^2 \cdot \sigma^2 \cdot \bar{u} \cdot \left(\frac{E}{RT} + 1 \right) e^{-E/RT}$$

where \bar{u} is the root mean square velocity.

²⁴⁾ Z. Physik 9, 216 (1922)

that the minimal duration of the active state required lies between 10^{-8} and 10^{-10} seconds, which is compatible with the estimates of duration of the active life based on such phenomena as fluorescence, decay of canal rays and width of spectrum lines, (cf. Sternand Volmer²⁵); Turner, (calculation on data of Cario and Franck and also of Wood)²⁶ and especially Tolman²⁷).

Let us now turn to a more general treatment regarding the source and mechanism of activation. You are probably aware that there exist two views, usually regarded as being in sharp opposition to one another, as to how the necessary preliminary transfer of energy to the molecule is effected. These views are respectively the *radiation hypothesis* and the *collision hypothesis*.

On the radiation hypothesis the molecule is supposed to pick up energy in the form of radiation from the space or field around it, this space being interpenetrated by radiation corresponding in respect of energy density and of distribution of energy among wavelengths to the temperature of the enclosure in which the molecules are contained.

On the collision hypothesis, it is denied that any sensible amount of energy can be drawn from the radiation field; instead it is by collisions with other molecules present in the system. So far as I can gather, the energy that is considered as being transferred and changed into chemical potential energy is simply the kinetic energy of relative speed of approach of the two colliding molecules. If this is so, the collision hypothesis in its simplest form would be represented by equation (2) to which reference has already been made. The collision hypothesis owes its origin essentially to work such as that of Franck and his co-workers on resonance and ionisation potentials in gases where one is dealing with the transfer of energy brought about by a rapidly moving electron colliding with an atom or molecule of a gas. In such cases it is beyond dispute that the kinetic energy of the electron is the determining cause. The conditions under which chemical change usually occurs are however sufficiently different to make it necessary to examine the question more closely. It is at once evident that whatever the nature of the collisions may be they cannot be simply those given by equation (2) as this equation would, for the correct E value, lead to velocities that are only sufficient for bimolecular change. The production of active states by collisions must be due to cumulative effects in which internal energies, rotational and vibrational, contribute as well as the simple kinetic energy of translation.

Let us now turn to unimolecular reactions in gases, processes which should afford a far more crucial test of the two opposing views than is afforded by bimolecular reactions. In the first place I might mention that ~~of the two opposing views than is afforded by bimolecular reactions. In the first place I might mention that~~ the difficulty of finding a gaseous reaction which is truly unimolecular has given rise to the idea that such reactions in fact do not exist. This I think is simply avoiding the issue. It is true that at the present time

²⁵) Physik Z. 20, 183 (1919).

²⁶) Phys. Rev. 23, 464 (1924).

²⁷) Phys. Rev. 23, 693 (1924).

we only know of a single reaction, namely the decomposition of nitrogen pentoxide which apparently is unimolecular. As you are no doubt aware, the kinetics of this reaction were first examined by Daniels and Johnston²⁸) who observed the unimolecular velocity constant at a series of temperatures not far removed from room temperature. The observed critical increment is 24700 calories. Writing the observed velocity constant in the form

$$k = Se^{-E/RT}$$

the observed value is satisfied by $3.26 \times 10^{13} e^{-24700/RT}$.

In a later paper, Daniels, Wulf and Karrer²⁹) state that the reaction is highly and positively catalysed by a small amount of nitrogen peroxide, one of the products of the reaction. Quite recently however, Hirst³⁰) working in Sir J. J. Thomson's laboratory, states this is not the case and that the reaction is a truly unimolecular one. Hirst finds good agreement with the velocity constants and critical increment of Daniels but finds the reaction to be quite uninfluenced by nitrogen peroxide, argon, oxygen, and air.

The position is a somewhat confusing one at the moment. I think however, that we must face the fact that unimolecular processes in gases are really possible and that when represented by an equation of the Perrin form, viz.

$$k = Se^{-E/RT}$$

it is necessary to ascribe to S a value of the order 10^{13} to 10^{14} . It is remarkable that, as found by Lueck³¹), nitrogen pentoxide when dissolved in chloroform or carbon tetrachloride has almost the same velocity constant and the same critical increment as it has in the gaseous case. The collision conditions here, one would have thought, would be very different from that in the gas by itself. Parenthetically I would like to point out that other reactions in solution which may be reasonably regarded as unimolecular apparently also require a high value for S, namely of the order 10^{15} or more, depending on the nature of the reaction. With these numerical magnitudes in mind, let us consider more exactly the position of the two opposing hypotheses.

The collision theory for unimolecular change is generally regarded as finding its best expression in the work of Christiansen and Kramers³²). The theoretical considerations involved are of a most ingenious but somewhat speculative character. The considerations deal with a complex series of collisions. The final expression obtained by Christiansen and Kramers is

$$k_{\text{unimolecular}} = A \cdot \frac{p_2}{p_1} e^{-E/RT}$$

when p_2 and p_1 are the a priori probabilities of the activated and normal states and $1/A$ is the average life in the activated state. So far as the variation of the velocity constant with temperature is concerned the expression is quite satisfactory, being in fact of the same form as the familiar equation of Arrhenius. The theoretical considerations of Christiansen and Kramers do not permit of an a priori calculation of A.

²⁸) J. Am. Chem. Soc. 43, 53 (1921).

²⁹) Ibid. 44, 2402 (1922).

³⁰) J. Chem. Soc. 127, 657 (1925).

³¹) J. Am. Chem. Soc. 44, 757 (1922).

³²) Z. physik. Chem. 104, 451 (1923).

They simply point out that on comparing the expression with experiment the value to be attributed to A is of the order 10^{-14} seconds. Christiansen and Kramers do not seem to think a value of this order an impossible one if collisions be the source of the energy of activation but they lay strong emphasis, on the incompatibility with the requirements of the Correspondence Principle of such a value for the life of the higher quantum state if absorption of radiation be the source of the energy of activation. Further than this we do not seem to be able to get on the basis of the Christiansen Kramers theory. It is only right to point out, however, that, if collisions are significant at all, a complex collision theory, possibly somewhat similar in general idea to that of Christiansen and Kramers, has to be postulated to account for the existence of activated forms maintained in statistical equilibrium.

Thus let us take up collisions from the point of view of equation (2) which would seem to be a simple and straightforward way of expressing this theory if kinetic energy were alone to be considered. Evidently on the basis of this equation we can calculate the maximum value which could be ascribed to the unimolecular velocity constant of chemical change if we equate the chemical rate, $k_{\text{uni}} \times N$, to the expression (2). In this way choosing as a specific example the decomposition of nitrogen pentoxide at one atmosphere say, and at 25° , it is found that

$$k_{\text{uni}} = 5.6 \times 10^{10} e^{-E/RT}$$

Obviously the factor 10^{10} is too small. It is because of this discrepancy that Christiansen and Kramers discarded the simple collision theory underlying equation (2) and endeavoured to allow for a more complicated series of collisions.

Let us now turn the bearing of the radiation hypothesis of activation upon unimolecular reactions. In the first place, if we adopt Planck's oscillator and apply his theory of continuous absorption then, as I showed several years ago, the calculated value of the unimolecular constant is exceedingly small compared with the observed. Taking the case of nitrogen pentoxide decomposition, it is thus calculated that at 25°

$$k_{\text{uni}} = 1.7 \times 10^7 e^{-E/RT}$$

$$k_{\text{uni observed}} = 3.26 \times 10^{13} e^{-E/RT}$$

In view, however, of the substitution by Einstein of a generalised Bohr model (Einstein³³) in place of the Planck oscillator even for the deduction of Planck's radiation law, one is naturally led to ask that sort of result may be obtained on this basis. This has been done by McKeown³⁴) who finds that

$$k_{\text{uni}} = \frac{p_2}{p_1} \nu e^{-h\nu/kT} = \frac{p_2}{p_1} \nu e^{-E/RT}$$

this result also containing the sheer assumption that the duration of the molecule in the active state is comparable with the reciprocal of the frequency of the radiation which is supposed to cause the activation. Since the ratio p_2/p_1 (the a priori probabilities of the two quantum states) is of the order unity, McKeown's expression is sensibly identical with the well known empirical expression of Dushman which approximately fits the observed facts. Whether this agreement is accidental or not is another matter.

³³) Physik. Z. 18, 121 (1917).

³⁴) Phil. Mag. 46, 321 (1923).

The criticism of the McKeown treatment has to do, however, with the assumption which he makes, namely that the duration of the active or higher quantum state in a generalised Bohr molecular model, in only of the order $1/\nu$, a quantity which is in contradiction to all previous estimates of the average life in the activated state and therefore contrary to the correspondence principle.

The argument which I have just been pursuing may perhaps be made more convincing by the following consideration of an actual case. Let us take the case of nitrogen pentoxide at normal temperature and pressure. The number of molecules per cc. is 3×10^{19} . From the experimental measurements it is found that at 0° C. a fraction 8×10^{-7} decompose per second. The actual number of molecules decomposing per second per cc. is therefore 2.4×10^{13} .

Now let us imagine as a condition the most favourable conceivable for the radiation hypothesis that the cc. of gas is represented by a thin fissure or crevice in a black body, the crevice being only 10^{-8} cm. thick, the opposing walls being 10^8 square cms. in area. On the basis of temperature radiation, we can calculate the amount of radiation of the required frequency which is emitted from the wall into the thin layer of gas per second. This is given by

$$2 \times 10^8 \times \frac{\pi h \nu^3}{c^2} e^{-h\nu/kT} d\nu,$$

where the refractive index has been taken as unity.

For nitrogen pentoxide ν calculated from the temperature coefficient is 2.6×10^{14} . The value of $d\nu$ obtained from observations on the width of lines is of the order 10^{11} (cf. Tolman, *loc. cit.*) Since one quantum $h\nu$ decomposes one molecule of nitrogen pentoxide the above expression gives for the number of molecules decomposed in the cc. per second the value 7.2×10^7 . (This is equivalent to saying that the velocity constant = $1.5 \times 10^8 e^{-E/RT}$.) Even if we take the width $d\nu$ to be 10^{14} instead of 10^{11} we only obtain a value 7.2×10^{10} , similar in magnitude to the value obtained by integrating for all frequencies greater than $\nu = 2.6 \times 10^{14}$. Obviously the maximum value which could possibly be obtained from thermal radiation is only a small fraction of the observed rate. The radiation hypothesis is therefore inadequate if the refractive index close to the band centre is of the order unity. It may perhaps be mentioned that at extremely high temperatures and in such systems as celestial bodies where the density of material is extremely small, and where nevertheless some kind of chemical change is not precluded, under such extreme conditions as these a radiational mechanism is probably applicable. We are not concerned with such conditions however in the present discussion.

The attempt has been made by McKeown and the writer to account for the observed rate of unimolecular change in terms of radiation on the basis of a greatly enhanced refractive index close to the centre of a band and very rapidly falling to normal values³⁵).

The best formulation — or perhaps I should say the least unsatisfactory formulation — of the radiation hypothesis would appear to be that of Rice³⁶); according to which there is a possibility of local con-

³⁵) cf. J. Am. Chem. Soc. 43, 1288 (1921).

³⁶) Phil. Mag. 1923, cf. also Lewis, „System of Physical Chemistry”, Vol. III, 3rd. Edition, 1924, Page 233.

densation of radiational energy in the immediate neighbourhood of molecules of matter. On this basis the numerical discrepancy may apparently be accounted for.

Leaving the radiation hypothesis, we have now to return to the collision hypothesis which in so far as it has yet been brought, it still far from satisfactory. The essence of the collision hypothesis for unimolecular change is that the rate of activation by collision must be greater than the rate of chemical decomposition of the resulting activated individuals, which means, of course, that de-activation without chemical change is going on at a rate comparable with the rate of activation itself. Active states in unimolecular processes are envisaged as physical realities.

Now it seems to me that whether activation is brought about by absorption of radiation or by collisions, the concept of an active state must be essentially the same sort of thing. The physicist's concept of an active state is a higher quantum state in a Bohr model. We have seen, however, that the life or duration of a Bohr higher quantum state is so great it would seem likely that it of itself can have little or nothing to do with unimolecular chemical change which consists essentially in the separation of two atomic or nuclear systems initially bound together by two (or at least a very small number) of so-called valency electrons. The commonly accepted view of what happens on dissociation of a diatomic gas is represented in Figure 3.

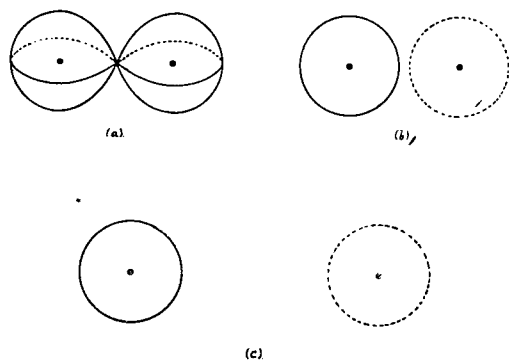


Figure III.

To account for unimolecular change and at the same time to retain the concept of activated state (which we must retain if a collision mechanism is the origin of energy transfer), then it is necessary to believe that something happens to an activated molecule whereby suddenly, and not in the relatively leisurely manner associated with de-activation by fluorescence, the molecule undergoes a change which results in the separation of its parts. In order to obtain this as a unimolecular effect it is necessary to regard the sudden alteration in the activated molecule as produced not by a further collision (which would lead to the square of the concentration of the gas and not its first power) but to some other cause. Here one naturally thinks of a part that may be played by radiation, not as actually contributing energy but acting in the sense of the old idea of trigger action.

In approaching the question of the possible nature of the condition which determines the disruption of the activated molecule, it is almost certain that we must look for some effect which could not occur in the case of a mononuclear system, but which is closely

connected with the fact that a molecule is essentially multinuclear. This in turn suggests that we must pay more attention to the relative motion of the nuclei (say in a diatomic gas) than is done (or can be done) in the ordinary treatment of the Bohr Model. In the same connection the suggestion of Franck to explain the existence or non-existence of absorption bands forces itself upon our notice as being probably capable of application. It will be recalled that Franck's suggestion is that the energy, represented by a higher quantum state on the part of the electrons may be transformed into molecular vibrations or motions of the nuclei.

Let us consider more particularly the case of nitrogen pentoxide which is the case for which the data are presumably the least unreliable. The observed velocity constant requires in this case that the term outside the exponential which we may conveniently denote by ν' is definitely different from the frequency ν which corresponds to the extent of the activation. In fact the value of ν' suggests a frequency such as would be attributed to the nuclear vibration in order to account for the vibrational part of the molar heat of the gas, as for example in Bjerrum's treatment. This suggests in turn that the radiation operative in the trigger action is that which is capable of initiating nuclear vibration and presumably even a single vibration occupying a time of the order 10^{-13} to 10^{-14} seconds would serve to displace the nuclei sufficiently to create the semi-catastrophic disturbance of the orbit of the valency electron and permit the application of the idea of Franck. If there is anything at all in this idea, one would be led to expect in general that the lower the molecular heat the higher should ν' be, i. e., the more complex the molecule in general the greater its molecular heat and the lower the value of ν' . It is only right to point out, however, that in the case of unimolecular reactions in solution so far as the data can be relied upon, one obtains values of ν' which vary with the solvent and the solute from 10^{13} or less to 10^{15} or more. The latter value can scarcely be attributed to nuclear or atomic vibration.

We have considered briefly the difficulties presented by the two opposing views of unimolecular chemical change, namely the radiation theory and the collision theory. A passing reference ought to be made to a view suggested by Langmuir³⁷), namely that the energy required for the spontaneous decomposition of a molecule is to be sought, not in an external source, but within the structure of the molecule itself — analogous to "Zero point energy".

External agencies simply act to set this free. This heats of reaction (e. g. $2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$) which are so great that it is impossible to account for them except by drawing upon a zero point energy. This was pointed out by the writer in 1917³⁸).

We have now considered a few aspects of the problems involved in chemical reactivity. It is fairly obvious, I think, that further progress on the theoretical side must await the extension of the quantum theory to multinuclear systems. The chemist in fact deals with systems which are more complex than any as yet envisaged by the mathematical physicist.

Liverpool, The University.

³⁷) J. Am. Chem. Soc. 42, 2190 (1920).

³⁸) W. C. M. Lewis, J. Chem. Soc. III, 461 (1917).

BOEKAANKONDIGINGEN.

678

Kurt Gottlob, *Technologie der Kautschukwaren*; Zweite Auflage; Vieweg, Braunschweig, 1925; 340 pgs., prijs gebonden f 13.75.

Bij de snelle ontwikkeling van de rubberwetenschap valt het niet te verwonderen, dat de in 1915 verschenen eerste druk van Gottlob's boek thans verouderd is. Het is daarom ten zeerste toe te juichen, dat de schrijver een geheel omgewerkten tweeden druk heeft doen verschijnen.

Het boek is in twee deelen gesplitst. Het eerste deel behandelt de algemeene rubbertehnologie t.w. eigenschappen van latex, winning, wasschen en drogen der ruwe rubber, de beteekenis der nevenbestanddeelen (harsen, eiwitten), de physische eigenschappen van de ruwe rubber, het mengen, theorie der vulstoffen, theorie van het vulcanisatieproces, de technische uitvoering daarvan, de versnellers, eigenschappen van de ge vulcaniseerde rubber en tenslotte een kort hoofdstuk over synthetische rubber.

Het tweede deel bevat een aantal capita selecta betreffende de fabricage van rubberartikelen, t.w. van rubberartikelen met en zonder weefsels, rubberzolen en -hakken, kinderspeelgoed, banden, rubberschoenen, eboniet, Paraband (patentgummi) en naadlooze rubberartikelen.

Het boek is up to date en kan in het algemeen warm worden aanbevolen. Het eerste deel is vergelijkbaar met het bekende boek van Luff. Betreffende dit deel dient echter opgemerkt te worden, dat de resultaten van diverse onderzoekingen niet steeds juist zijn verwerkt en hier en daar besliste onjuistheden zijn ingeslopen. Ook bevatten de namen van niet Duitsche onderzoekers vele drukfouten, zoowel in den tekst als in het register.

Het tweede deel is zonder twijfel de beste beschrijving van de fabricage van rubberartikelen, welke in de literatuur is te vinden en bevat een schat van wetenswaardigheden. Het is een tragische gedachte, dat dit werk de laatste pennevrucht van den schrijver is geweest, welke op 43-jarigen leeftijd kort na het verschijnen van dezen tweeden druk overleed.

A. van Rossem.

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678(022)

Manuel de l'industrie du caoutchouc par A. Chaplet; Baillièrè, Paris 1925; pg. 247, prijs f 1.80.

Het doel van dit boekje is, een overzicht te geven van rubberchemie en technologie, doch helaas laat de bewerking der stof veel te wenschen over.

Achtereenvolgens worden behandeld de grondstoffen van de rubberindustrie, t.w. ruwe rubber (bereiding en eigenschappen), regeneraat, factis, vulstoffen en katalysatoren, de diverse bewerkingen, welke in de rubberfabrieken plaats vinden (wasschen, drogen, mengen, kalanderen, vulcaniseeren), terwijl daarna de beschrijving volgt van de fabricage van een aantal rubberartikelen. Het boek besluit met hoofdstukken over analyse en keuring van rubberartikelen en over guttapercha, balata en chicle.

Deze indeeling is te waardeeren, doch de behandeling der stof is oppervlakkig en onevenwichtig, hetgeen uit enkele voorbeelden moge blijken.

Op pg. 11 wordt een verbruiksstatistiek van rubber gegeven van het jaar ... 1914; het verbruik van ruwe rubber in de Vereenigde Staten is sindsdien verviervoudigd. Bij de bereiding van ruwe rubber op pg. 23-28 worden talrijke bizarre inlandsche methoden besproken, doch een bespreking van de gewone bereidingswijze van crepe en sheet ontbreekt. De classificatie van ruwe rubbers heeft blijkbaar slecht betrekking op Braziliaansche rubber, plantagerubber wordt niet vermeld. Men krijgt den indruk, dat de schrijver onbekend is met het feit, dat 95% van alle rubber, welke aan de markt komt,

op de plantages is bereid. Bij de constitutie van rubber wordt weer melding gemaakt van de onjuiste formule van Harries uit 1911. De paragraaf over de eigenschappen van rubber laat alles te wenschen over.

Geen studieboek voor insiders, maar evenmin een boek om in handen te geven aan hen die zich willen oriënteren.

A. van Rossem.

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66/022

Mechanical Mixing Machinery by Leonard Carpenter, Benn Brothers, London, 1925; 138 pgs., prijs 6/—.

Dit boekje, blijkens de voorrede geschreven voor „the student of chemical engineering, and to the young works chemist anxious to study the art of transferring a laboratory process to the works” is van een oppervlakkig karakter en zal om die reden niet aan zijn doel beantwoorden. Achtereenvolgens worden besproken de methoden van menging en de typen van mengmachines. De laatste hoofdstukken zijn gewijd aan het mengen in speciale industrieën t.w. de cement-, de aardwerk- en de kunstmestindustrie, terwijl een aantal andere industrieën in een laatste hoofdstuk zijn samengevat. Eenige actualiteit is aan het boekje gegeven door een hoofdstuk betreffende het mengen met behulp van kolloïdmolens, waarvan de Plauson- en de Premier-kolloïdmolen worden besproken.

Het geheel blijft, zoals reeds opgemerkt, erg aan de oppervlakte en is naar het oordeel van Ref. meer geschreven voor den leek, welke zich eens wenscht te oriënteren, dan voor den student in chemische technologie. Het is vooral te betreuren, dat de schrijver heeft verzuimd te verwijzen naar beter en uitvoeriger literatuur, zoodat dit boekje evenmin als eerste wegwijzer op dit gebied kan worden aanbevolen.

A. van Rossem.

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631.121:541.12(022)

Base Exchange in Soils, General Discussions held by the Faraday Society, Gurney & Jackson, Paternoster Row, London, E. C. 4, prijs f 3.50.

De Faraday Society in Londen heeft het zeer toe te juichen initiatief genomen, om van tijd tot tijd over een onderwerp, dat algemeen belangstelling trekt, een bespreking en discussie tusschen de daaraan werkende onderzoekers te organiseeren. Het onderwerp wordt ingeleid door een der sprekers en zijn voordracht, gezamenlijk met de mededeelingen van de andere sprekers en de gehouden discussie tot een afzonderlijk verkrijgbare publicatie van de F. S. vereenigd.

Het onderwerp van de bijeenkomst in December 1924 droeg bovenstaanden titel en werd ingeleid door D. J. Hissink, die daarin een exposé gaf van den stand van het vraagstuk en van de onderzoekingen, die daaromtrent in de afgelopen jaren onder zijn leiding in de 3e afd. van het R. L. Proefstation in Groningen zijn verricht. De adsorptie in den bodem, bijv. van K-zouten, berust op de stoichiometrische uitwisseling met andere basen, vooral Ca, die in uitwisselbare vorm aan de klei of humus gebonden zijn. De hoeveelheid der op dergelijke wijze uitwisselbare basen (in aequivalenten uitgedrukt: S) is voor de beoordeeling van een grondsoort van veel beteekenis.

Daarnaast is een andere factor van belang, de zgn. graad van saturatie V. Bij vele grondsoorten, vooral die, welke arm zijn aan CaCO₃ of waarin dit ontbreekt, kan nl. door behandeling met Ca(OH)₂ of Ba(OH)₂ de hoeveelheid uitwisselbare basen vergroot worden tot een maximumwaarde T. De graad van saturatie is nu $V = 100 \frac{S}{T}$.

Hissink heeft op deze factoren bij de beoordeeling van den grond de aandacht gevestigd en methoden aangegeven, om ze te bepalen,

Page and Williams en Robinson en Williams passen deze methoden toe op Engelsche gronden en doen mededeeling van hun proeven daaromtrent op de proefvelden te Rothamsted en in Wales. De eersten komen tot het resultaat, dat in gronden met overmaat CaCO_3 de hoeveelheid uitwisselbare basen in direct verband staat met de hoeveelheid zeer fijn anorganisch materiaal en humus. Verder artikelen van Fischer, Saint en Comber.

Voor ieder, die belang stelt in het adsorptievraagstuk, speciaal voor andere adsorbentia dan kool, zijn deze onderzoeken van veel belang en kan de lezing daarvan zeer worden aanbevolen.

W. Reinders.

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5301:16(022)

La théorie de la relativité restreinte d'Einstein et la Logique, 20 bldz., Dr. J. H. Tummers (6 Hoogeweg, Venlo).

Eene vertaling van het reeds vroeger (Chem. Weekblad 22 Nov. 1924) door ons aangekondigde „Die spezielle Relativitätstheorie Einsteins und die Logik“. De auteur heeft er echter eene „Réponse à quelques objections“ aan toegevoegd.

Dit laatste naar aanleiding van eene in „Nature“ voorgestelde oplossing om uit de logische impasse der theorie te geraken door de relatieve tijd als postulaat te stellen. Het postuleeren is hier volgens Dr. Tummers logisch ongeoorloofd, terwijl bewijzen logisch onmogelijk is.

Den lezers, wien dit interesseert, kan ik nog mededeelen, dat onlangs in het tijdschrift „De Nieuwe Eeuw“ van mijn hand eene afleiding van de Einsteinsche secundevergrooting verscheen, die duidelijk laat uitkomen, dat deze vergrooting moet dienen om eene van de werkelijkheid afwijkende vooropstelling te compenseeren, en als zoodanig ook van de werkelijkheid moet afwijken, dus zuiver fiktief is, hoewel als rekenkundig hulpmiddel toelaatbaar. Einstein's fout is, dat hij haar voor reëel aanziet. Men kan voor de berekening van den reisduur, voor een afstand, die tijdens de reis grooter wordt, aannemen, dat deze afstand onveranderd blijft, maar de snelheid naar verhouding kleiner wordt. Wie nu aanneemt, dat men dus langzamer reist, maakt wezenlijk dezelfde fout als Einstein, die beweert, dat een klok door beweging langzamer gaat loopen.

Mijn artikel had tot opschrift: „De proef van Michelson, relativiteit en werkelijkheid“ en is inmiddels als brochure „De Fout van Einstein“ uitgegeven door Harte, Bergen op Zoom.

W. Tombrock.

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612.015.1

Carl Oppenheimer, Die Fermente und ihre Wirkungen, nebst einem Sonderkapitel: Physikalische Chemie und Kinetik, von Richard Kuhn; fünfte, völlig neu bearbeitete Auflage; Georg Thieme Verlag, Leipzig, 1924/1925. Lieferung IV, blz. 480—640; Lieferung V, blz. 640—775, prijs M. 10.20.

Met deze vierde en vijfde aflevering wordt het eerste deel van bovengenoemd werk beëindigd. Behalve een klein deel der vierde aflevering, dat nog het laatste gedeelte der esterassen behandelt en een veertiental bladzijden van aflevering V, waarin de nucleasen besproken worden, zijn beide afleveringen gewijd aan de carbohydrasen, waarbij niet alleen aan de fermentwerkingen de noodige aandacht is geschonken, doch tevens aan de chemie der polysen, zoover deze thans door het werk van Karrer, Pringsheim, Haworth, Irvine, Pictet, e.a. is ontwikkeld. Tevens mogen speciaal genoemd worden de synthetische onderzoeken van Bourquelot en de fermentstudien van von Euler, Willstätter en Kuhn, die alle uitvoerig worden besproken. Gaarne wenscht referent deze voortreffelijke samenvatting dan ook in veler handen.

C. F. van Duin.

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662.2(021)

Spreng- und Zündstoffe, von Prof. Dr. H. Kast; Vieweg, Braunschweig, 1921; 548 blz.

Het standaardwerk van Guttmann over ontplofbare stoffen is langzamerhand geheel verouderd. Een herziening van dit eens zoo voortreffelijke werk werd daarom zeer gewenscht en het valt toe te juichen, dat een zoo alleszins bevoegde als Kast dezen arbeid op zich heeft genomen en met succes heeft beëindigd. Het thans verschenen werk behandelt de ontplofbare stoffen in uitgebreiden zin, de ontstekingsmiddelen en de lustvuurwerkerij. Een belangrijke plaats is ingeruimd voor de bespreking van de theoretische en practische beoordeeling der ontplofbare stoffen. Een overzicht van den inhoud van dit werk zou hier te veel plaats vergen. Er zij slechts vermeld, dat een zeer groot materiaal op deskundige wijze is verwerkt. Een uitgebreide literatuuropgave verhoogt nog de waarde van dit voortreffelijke werk. Hoewel de typografische verzorging overigens goed is, moet worden betreurd, dat niet een betere kwaliteit papier is gebruikt.

G. de Bruin.

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661.26(021)

Absorption of Nitrous Gases, by H. W. Webb, M.Sc., F. I. C. London; Edward Arnold & Co., 1923, 372 blz., 25 sh. net.

Dit boek behandelt hoofdzakelijk de absorptie van nitreuze gassen door water, zoowel van theoretisch als van industrieel standpunt gezien. Andere methoden, als de terugwinning met alkaliën of met zwavelzuur, worden slechts zeer terloops vermeld. Nu moet worden erkend, dat de absorptie door water verreweg de belangrijkste is en deze methode wordt in dit werk op zeer grondige wijze behandeld. Na een overzicht over de verschillende stikstofoxyden, wordt de theoretische zijde van het vraagstuk gezien. Vervolgens worden de absorptietorens en de gas- en zuurcirculatie met bijbehorende apparatuur behandeld, waarna volgt de concentratie van het slappe salpeterzuur, benevens de vervaardiging van nitraten en nitrieten. Tot besluit een hoofdstuk over de analytische controle van het bedrijf.

De typografische verzorging van dit werk is voortreffelijk.

G. de Bruin.

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666.76(022)

Ob.-Ing. L. Litinsky, Schamotte und Silika, ihre Eigenschaften, Verwendung und Prüfung; 286 pag.; 75 fig.; 43 tab.; Verl. Otto Spamer, Leipzig, 1925; 27 GM. geb.

Litinsky, die voor korten tijd de technische litteratuur heeft verrijkt met een afzonderlijk tijdschrift op het gebied van de vuurvaste materialen, heeft thans zijn groote ervaring en kennis op dit speciale terrein neergelegd in een boek. In de voorrede deelt hij mede, daarbij te zijn uitgegaan van de gedachte, dat er weliswaar een overvloed van werkjes zijn, die de vervaardiging van vuurvaste steenen behandelen, doch dat er gebrek zou zijn aan een werk, dat deze materialen behandelt van uit het standpunt van den verbruiker. Wij onderschrijven deze meening volkomen, en juichen dan ook het verschijnen van het boek van Litinsky van harte toe, dit te meer, daar de bewerker naar onze meening in zijn pogen zoo voortreffelijk is geslaagd. Veel, dat tot nu toe slechts in weinig toegankelijke speciale litteratuur was te lezen, is hier bijeen gebracht en tot een werkelijk geheel verzameld en opgebouwd. Zonder de betekenis van de theoretische grondslagen op dit gebied vooralsnog te overschatten, heeft de schrijver toch deze als leidraad weten te behouden. Het zal dan ook eerder stimulerend werken op nader wetenschappelijk onderzoek, dan den indruk vestigen, dat de zaak „al voor elkaar is“. Te be-

treuren is, dat de schrijver blijkbaar niet de beschikking heeft gehad over het Journ. of the Amer. Ceramic Soc., waarin toch zooveel uiterst belangrijke onderzoekingen op vuurvast gebied zijn verschenen. Mede daardoor maakt het werk wel ietwat den indruk van eenzijdig Duitsch te zijn, hoewel dient te worden erkend, dat veel Engelsch werk wel is opgenomen. Overigens kunnen wij dit werk met veel genoegen aanbevelen aan de groote groepen van ingenieurs, die bij vuurvaste materialen belang hebben.

C. J. van Nieuwenburg.

CHEMISCHE KRINGEN.

Leidsche Chemische Kring. Den 19den Augustus is te Leiden overleden Dr. P. J. Montagne, eerevoorzitter van den Leidschen Chemischen Kring, die 16 December 1908 door hem en Dr. G. L. Voerman is opgericht en dien hij tot Mei 1917 als voorzitter heeft geleid.

De voordrachten, door hem in een tiental vergaderingen gehouden, waren steeds uitnemend voorbereid. Vier er van werden, op verzoek der redactie, bewerkt tot verhandelingen voor het Chem. Weekblad. Vele van de door hem in die vergaderingen uitgesproken denkbeelden en medegedeelde experimenteële resultaten vindt men terug in zijn publicaties, verschenen in het Rec. trav. chim.¹⁾

De titels der voordrachten zijn:

Sterische hindering bij aromatische verbindingen (14 Jan. 1909).
Aanvullende mededeeling over sterische hindernissen bij organische verbindingen (10 Juni 1909).

Het kleurloos worden van alcoholische kali in het licht (10 Juni 1909).

Scheikundige veranderingen van organische verbindingen onder den invloed van het licht (3 Maart 1910).

„Beckmann'sche Umlagerung” bij eenvoudige eenwaardige oximen (2 Nov. 1911).

Friedel-Crafts' synthese van aromatische koolwaterstoffen en ketonen (11 Nov. 1913).

Over eigenaardige oxydatie van joodtoluol (7 April 1914).

Intramoleculaire verhuizing van de phenylgroep (15 Maart 1918).

Labelele atoomgroeperingen bij organische verbindingen (19 Febr. 1919).

Los en vast gebonden atomen en groepen in organische verbindingen (18 Maart 1920).

De werking van alcoholische kali op broombenzophenonen (20 Maart 1923).

De aangename, rustige en zakelijke wijze, waarop Montagne de vergaderingen van den Kring heeft geleid, zal blijven leven in de herinnering der leden, en niet minder datgene wat hij buiten de vergaderingen voor den Kring heeft gedaan.

Bij de begrafenis was de Kring vertegenwoordigd door den secretaris en eenige leden (voorzitter en penningmeester waren buitenslands).

PERSONALIA, ENZ.

Dr. P. J. Montagne †. Bij de begrafenis waren o.a. aanwezig de hoogerleraren Ehrenfest en van der Woude, Dr. P. Aug. Driessen, Dr. Voerman, Dr. Moll van Charante en andere vrienden van den overledene; verder assistenten en personeel van het organisch-chemisch laboratorium, studenten en andere belangstellenden.

Allereerst werd het woord gevoerd door Dr. G. L. Voerman. Deze zeide:

„Het Bestuur van de Nederl. Chem. Vereeniging heeft mij verzocht, om bij deze droeve plechtigheid de Vereen. te vertegenwoordigen en om namens haar een laatste groet te brengen aan een medelid, waaraan de Vereeniging veel te danken heeft. Montagne toch heeft gedurende zijn werkzaam leven ook zeer veel diensten aan de Nederl. Chem. Vereeniging bewezen, waarvan wel de voornaamste is, dat hij gedurende vijf jaren het secretariaat heeft vervuld. En hij heeft dit gedaan op een wijze, die in hooge mate tot den vooruitgang der Vereeniging heeft bijgedragen. Secretaris geworden in een tijd, dat de Vereeniging nog betrekkelijk klein was, heeft hij het medegemaakt en medebewerkt, dat nieuwe banen werden ingeslagen, waardoor de Vereeniging tot grooten bloei kwam. Zeker is hij niet alléén de bewerker daarvan

¹⁾ Zie Chem. Weekblad 21, 589—591 (1924).

geweest, doch wij weten allen, welk een kracht in een bestuur van een goed secretaris kan uitgaan. En indien Montagne in dien tijd niet de bekwame en onvermoeibare werker was geweest, wien niets te veel was en die steeds bereid was om al zijn weten en kunnen in dienst der Vereeniging te stellen, ware zeker niet dat alles bereikt, wat in die jaren is verkregen. Daarbij was in Montagne iemand getroffen, die aan groote wetenschappelijkheid ook praktischen zin paarde. Zelf heb ik het voorrecht gehad, om nog een enkel jaar van zijn secretariaat in nauw verband met hem voor de Vereeniging samen te werken, en zijn helder oordeel, onvermoeide zorg, groote bekwaamheid en werkkraft zullen mij daarvan bijblijven. Ook na het nederleggen van zijn secretariaat, nu ruim drie jaren geleden, bleef zijn belangstelling uitgaan naar alles wat met de Vereeniging verband hield, al maakte zijn gezondheidstoestand, dat wij hem niet meer zoo geregeld als voorheen op de vergaderingen zagen; toch heeft hij nog vaak van advies gediend en werkte hij mede aan de tijdschriften der Vereeniging. Tot het laatst toe was hij een werkzaam redactielid van een der tijdschriften en droeg daardoor nog steeds bij tot verspreiding van den goeden naam en faam der Nederlandsche chemici en der Vereeniging. Namens de Nederl. Chem. Vereeniging breng ik hier eerbiedig hulde aan de nagedachtenis van Dr. P. J. Montagne, die zooveel voor de Vereeniging deed.

„Het moge mij vergund zijn, om als vriend van den overledene nog een enkel woord hieraan toe te voegen. Mijn kennismaking met Montagne dateerde reeds van omstreeks 1900 en toen het teval onze wegen in 1907 te Leiden te zamen voerde, duurde het niet lang, of ik mocht mij in de vriendschap van Montagne en zijn vrouw verheugen. Steeds zal ik aan die vriendschap, aan het gelukkige en gastvrij gezin de beste herinneringen bewaren. Hoewel Montagne's levenspad lang niet altijd over rozen ging en teleurstellingen, waarbij onzes inziens zeer onverdiende, hem niet bespaard bleven, was hij voor zijn vrienden steeds dezelfde. Blijmoedig diende hij de wetenschap, die hem zoo lief was; steeds was hij bereid zijn vrienden en anderen behulpzaam te zijn, hen van zijn groote kennis mede te deelen en zich in te denken in de bezwaren en vraagstukken van anderen. Wij kunnen ons voorstellen, wat zijn vrouw en zijn familie door zijn heengaan verliezen; moge het hun daarbij tot een geringe troost zijn, dat ook zijn vrienden door zijn heengaan diep zijn getroffen en dat zij de beste herinnering aan hem zullen houden. Hij ruste in vrede”.

Daarna sprak Dr. J. Moll van Charante, een der oudste vrienden, eenige woorden van grooten dank voor de jaren van trouwe en onbaatzuchtige vriendschap, die Dr. Montagne hem geschonken had.

Dr. J. van Alphen, sprekende namens assistenten, doctorandi en candidaten van het organ.-chem. laboratorium, wees op de groote belangstelling, die Dr. Montagne steeds voor hun studie had getoond. Hij was op de hoogte van den stand van ieders werk. Mede door zijn grootc experimenteële vaardigheid, wist hij raad voor bijna elke moeilijkheid, die zich voordeed. Zijn wijze van werken was ideaal en strekte hun allen tot voorbeeld.

Dr. W. J. van der Lee (Apeldoorn), zwager van den overledene, dankte namens de familie voor de betoonde belangstelling.

Er waren kransen, o.a. van de Nederl. Chem. Vereeniging, van den Leidschen Chemischen Kring, van den hoogleeraar-directeur, assistenten en studenten van het laboratorium en van het personeel daarvan en vele bloemen.

* * *

Te 's-Gravenhage is 26 Augustus in den ouderdom van 93 jaar overleden Prof. Dr. R. S. Tjaden Modderman, oud-hoogleeraar aan de Universiteit te Groningen, waar hij in 1893 door Prof. Holleman werd opgevolgd. In het Chem. Weekblad van 23 Juni 1917 verscheen een levensbericht, vergezeld van een bibliographie, in verband met zijn 60-jarig doctoraat.

* * *

Op 11 December a.s. zal het 50 jaar geleden zijn, dat Prof. Dr. H. A. Lorentz, eerelid der Nederl. Chem. Vereeniging, tot doctor in de wis- en natuurkunde werd bevorderd aan de Universiteit te Leiden. Over de Commissie, die zich naar aanleiding hiervan heeft gevormd, zullen wij eerstdaags een mededeeling opnemen.

CORRESPONDENTIE, ENZ.

De hoofdredacteur heeft 25 Augustus zijn werkzaamheden hervat. Indien men op 1 September nog niet antwoord mocht hebben ontvangen op tot hem gerichte vragen, gelieve men opnieuw te schrijven.