

The so-called 'thermokalite' and the existence of sodium bicarbonate as a mineral.

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IN a brief account of the Johnston-Lavis collection of Vesuvian minerals, now preserved in University College, London, Dr. K. W. Earle mentions 'a large number of specimens of "Thermokalite", a new member of the Haloid group, which has, apparently, so far escaped description.'¹ This previously unpublished name was copied from Dr. Johnston-Lavis's manuscript labels. The late Dr. H. J. Johnston-Lavis (1856-1914) possibly considered that this mineral was the potassium compound corresponding to thermonatrite [$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$]. A provisional name for an undetermined mineral having, in this way, unfortunately been published, it seemed desirable to clear up the matter. For this purpose Dr. Earle very kindly supplied two good specimens of the mineral for investigation. Access was also given to the note-books kept by Dr. Johnston-Lavis. He had made a separate entry for each specimen and the carbon copies were placed with the specimens. The entry for 'thermokalite' reads in every case: 'Thermokalite (n. sp.) by Tunnel nr. Stufe di Nerone, Baja.' This locality is situated about nine miles west of Naples in the Phlegrean Fields (Campi Phlegraei).

The name 'thermokalite' is not mentioned in the bibliography of Dr. Johnston-Lavis,² but a reference to the incrustations is made in a report to the British Association for the Advancement of Science in the year 1889. Dr. Johnston-Lavis acted as secretary to the committee which presented eleven reports on the investigation of the volcanic phenomena of Vesuvius and its neighbourhood to the British

¹ K. W. Earle, Proc. Geol. Assoc. London, 1928, vol. 39, p. 96. The name 'thermokalite' has been listed in Min. Mag., 1928, vol. 21, p. 578.

² H. J. Johnston-Lavis, Bibliography of the volcanoes of southern Italy. London, 1918.

Association during the years 1885-95. Reference is made in the report for 1886 (p. 228) to plans for the Cumana railway which was to connect Naples with Baia and Fusaro. The new railway would necessitate tunnelling the hill which backs Baia. In the report for 1888 (p. 322) it is noted that the entrance of this tunnel had been commenced just beneath the Baths of Nero (Stufe di Nerone) and considerable difficulties were anticipated owing to the high temperature of the rock. A full account of the tunnelling operations is given in the 1889 report (pp. 289-91). During excavations many *cuniculi* cut out by the Romans were found. These *cuniculi* are underground conduits just large enough to allow a man to pass, and were apparently made for the passage of the thermal spring water to the baths. In one of the principal *cuniculi* Dr. Johnston-Lavis found abundant saline incrustations varying from 1 to 10 cm. in thickness. These covered the walls of the tunnel for a considerable distance; under the incrustations a light brown friable tuff was found. The conditions of temperature and atmosphere had, of course, been affected by the increased ventilation afforded by excavation. However, the temperature observed in the principal *cuniculus* was 73° C., and Dr. Johnston-Lavis attributed the distressing physiological condition of his guide and himself after visiting this tunnel to the presence of considerable carbon dioxide in the atmosphere. Dr. Johnston-Lavis concluded from qualitative tests on these saline incrustations that the principal component was potassium carbonate. He observes that this salt appeared to be present in 'two, if not three different varieties of hydration'. He also found sodium present and small quantities of chloride and sulphate. Although it will be shown that these results are not confirmed by the present paper, there can be no doubt that the series of specimens labelled 'thermokomite' in the Johnston-Lavis collection are the incrustations that were collected and examined by Dr. Johnston-Lavis prior to this report of 1889.

A considerable quantity of the incrustation must have been collected, for we find 'thermokomite' very well represented in the Johnston-Lavis collection. About a dozen large specimens are shown in the case-tops. The largest and most beautiful of them measures approximately 30 × 24 × 6 inches; the remainder average about one-third of this size. Still smaller but quite excellent specimens are stored in two cabinet drawers.

The two specimens handed over for examination are about the size of one's fist, and consist of a snow-white friable material with some

pale yellow stains in places. There is no rocky matrix present on these specimens, but on one or two of the incrustations in the Johnston-Lavis collection the 'thermokalite' is covered on one side with a light brown powdery tuff. The surface of the two blocks is cavernous, but the interior is more compact and shows a fibrous structure. Bundles of minute needles line the cavities, and a preliminary microscopic examination of these crystals revealed the presence of thermonatrite and trona. The material dissolves readily and completely in cold water. Qualitative tests showed the presence of sodium sulphate and carbonate, a trace of iron, but no potassium or ammonium salts. No trace of a chloride could be detected; the addition of silver nitrate to a solution of about three grams of the material in nitric acid produced only a faint turbidity. It was thought that the crusts might vary in composition. Dr. K. W. Earle, therefore, kindly allowed me to take small specimens, each about five grams, from several other crusts in the Johnston-Lavis collection, for the detection of potassium. The most careful tests failed to reveal even a trace of this element; it was found, however, that the sulphate content varies considerably from one crust to another.

Trona $[\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}]$ is usually associated with thermonatrite and, as noted above, was detected in the preliminary microscopic examination. A small quantity of the mineral was therefore heated, and the gases evolved bubbled through clear baryta water. A heavy precipitate thus formed indicated the presence of bicarbonate in the original material. In order to gain some idea of the relative proportions of normal carbonate and bicarbonate, advantage was taken of the property of the indicator phenolphthalein to lose its colour in the presence of free carbon dioxide. Several samples of the mineral were dissolved in cold water and titrated with hydrochloric acid, using first phenolphthalein to determine the normal carbonate and then methyl-orange to determine the total carbonate content. For a mixture of thermonatrite and trona, if x be the quantity of acid added, using phenolphthalein as the indicator, then the quantity of acid that must be added to complete the titration with methyl-orange can never be greater than $2x$ and only equals $2x$ when no thermonatrite is present. With the given samples, the quantity of acid added in the second part of the titration was always greater than $2x$ and in many cases approached $3x$. The validity of this method of estimation was tested by titrating with the same strength of acid, and under the same conditions solutions of (1) pure

sodium carbonate, and (2) a mixture of equal molecular proportions of sodium carbonate and sodium bicarbonate. The experimental values agreed closely with theory; hence these preliminary titrations showed that free sodium bicarbonate must be present.

Three average samples were now picked out as representative of the whole mass and investigated quantitatively. Each sample, weighing one to two grams, was dissolved in cold water and titrated with a standard solution of hydrochloric acid using two indicators, phenolphthalein and methyl-orange, as described above. A few more drops of hydrochloric acid were added after titration, and the sulphate was precipitated from the hot, weakly acid solution as barium sulphate. The sodium carbonate, bicarbonate, and sulphate contents of the mineral were thus estimated and the water content deduced by subtracting the sum of these constituents from the weight of the original sample. Although no direct determination of the water content was made, support for the deduced figures was obtained by heating five other samples to a dull red heat. The average loss of weight due to evolution of carbon dioxide and water vapour was 21.3%. This agrees very well with the mean loss to be expected for the three samples analysed, namely, 21.5%. The values obtained for the water content are therefore sufficiently accurate. The analyses of the three samples are given below:

	1.	2.	3.
Na ₂ CO ₃	30.42	27.92	27.91
NaHCO ₃	32.42	37.65	39.66
Na ₂ SO ₄	29.68	25.89	24.57
	<hr/>	<hr/>	<hr/>
	92.52	91.46	92.54
H ₂ O (difference)...	7.48	8.54	7.86
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00

We have no means of finding out the exact temperature and state of humidity of the atmosphere under which the saline incrustations were formed, though we know from Dr. Johnston-Lavis's observations that the minimum temperature was 73° C., and that the atmosphere was very moist and probably contained appreciable carbon dioxide. We have to consider first whether the normal carbonate is present not only as thermonatrite and trona, but also as natron [Na₂CO₃.10H₂O]. It is known that under ordinary conditions natron is only stable below 32.5° C.; above this temperature thermonatrite, the mono-

hydrate, is the stable salt.¹ The vapour-pressure for the balanced system $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} + 9\text{H}_2\text{O}$ has been measured at various temperatures.² For natron to exist above 70° C. the vapour-pressure must be above 200 mm. From the above analysis it can be seen that there is not enough water to permit all the normal carbonate being present as trona. As a working hypothesis, therefore, it will be assumed that the partial pressure of the water-vapour was not sufficiently high for natron to be present. Similarly, hydrated sodium sulphate [$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$] under ordinary conditions does not exist above 32.6° C.,¹ and although data do not exist as to its vapour-pressure at high temperatures it is reasonable to assume also in this case that the sodium sulphate is present as the component thenardite [Na_2SO_4]. Finally, the analyses show that even if all the sodium carbonate be present as trona, a possibility denied by the insufficient water content, there would be a considerable amount of free sodium bicarbonate present. Hence it is probable that the analyses represent a mixture of thermonatrite, thenardite, trona, and sodium bicarbonate. The above considerations show that the possibility of the components mirabilite [$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$] and natron [$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$] being present is very small. In any case the amounts of these two minerals present must be negligible owing to the low water content. The figures below show the approximate proportions of the minerals assumed to be present in the original mixture.

	Thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$).	Trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$).	Sodium bicarbonate (NaHCO_3).	Thenardite (Na_2SO_4).
No. 1 ...	18	32	20	30
2 ...	7	47	20	26
3 ...	11	39	25	25

The above figures, showing the amounts of thenardite and thermonatrite in the ratio of 2:1 to 3:1, suggest the possibility of the presence of a double salt, such as $4\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ (hanksite) or $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$.³ This has been considered, but without definite results.

An optical investigation of the mixture was then resumed. The

¹ A. E. Dunstan and H. Langton, Journ. Chem. Soc. London, 1912, vol. 101, p. 419.

² A. F. Gerasimov, Journ. Russ. Physico-Chem. Soc., 1912, vol. 44, p. 1666.

³ W. A. Caspari, Journ. Chem. Soc. London, 1924, vol. 125, p. 2381; A. F. Rogers, Amer. Journ. Sci., 1926, ser. 5, vol. 11, p. 473. [Min. Abstr., vol. 3, p. 162.]

majority of the fragments, viewed under the microscope, give straight extinction with negative elongation. The maximum refractive index for some is 1.524 and for others just greater than 1.540. The latter correspond to trona and the former to thermonatrite. Trona was found not only in the compact mass but intergrown or cemented together with the thermonatrite crystals lining the cavities. Plentiful irregularly-shaped masses determined as thenardite were found, but no traces of minerals with all the refractive indices lower than 1.469 (olive-oil), such as natron or mirabilite. The thenardite in some places seems to consist of a transparent core surrounded by material which has effloresced. The remaining component was readily distinguished from all those above mentioned. Small crystals giving an extinction angle of 20° to an edge, the direction of which is negative, are found both in the compact mass and at the surface. They possess very high birefringence and the maximum refractive index is only a little less than 1.590. Artificially prepared sodium bicarbonate crystals were examined side by side and gave exactly the same characteristics. The chemical and optical data prove conclusively the presence of free sodium bicarbonate.

The results of analysis show that the amount of free sodium bicarbonate present cannot be less than 20%. An attempt was therefore made to concentrate this compound by separating the lighter and heavier components with mixtures of methylene iodide and benzene of varying specific gravities. Such a mixture was adjusted till a crystal of trona from Lake Magadi, Kenya Colony, just floated. Most of the 'thermokalite' introduced into the mixture floated just below the trona crystal. The smallest particles at the bottom of this layer were withdrawn and examined optically. They were found to contain a larger quantity of sodium bicarbonate than before separation, but most of the material seemed to be intergrown with trona or thermonatrite. Some crystals appear to have an interior of thermonatrite and an outer zone of sodium bicarbonate. Unfortunately even the larger crystals of sodium bicarbonate were easily visible only with a $\frac{1}{4}$ -inch objective; it therefore appeared unprofitable to attempt the more difficult separation of trona from the sodium bicarbonate. However, we may conclude that the specific gravity of the sodium bicarbonate is just greater than that of the trona crystals. Walther found the specific gravity of Lake Magadi trona to be 2.14.¹ The value for sodium bicarbonate is probably therefore nearer 2.2. It is interesting

¹ P. Walther, *Amer. Min.*, 1922, vol. 7, pp. 86-88. [*Min. Abstr.*, vol. 2, p. 47.]

to note that the specific gravity of artificial sodium bicarbonate crystals is 2.22.¹

Physically and chemically, then, the so-called 'thermokalite' would appear to be a mixture of trona, thermonatrite, sodium bicarbonate, and thenardite. The name 'thermokalite' is therefore unnecessary. The crusts vary considerably in sulphate content. In one case the amount of sodium sulphate falls to 4%, and the crust seems to be composed almost entirely of trona. So far as I am aware this is the first reported occurrence of such minerals from the Phlegrean Fields. The existence of sodium bicarbonate in these saline incrustations as a mineral will now be discussed.

It is mentioned above that trona has not been previously reported from Campi Phlegraei. Trona occurs both at Vesuvius and Etna, but complete analyses have not been published. V. R. Matteucci examined a white crystalline substance from Fosse Grande, Vesuvius, and found a large quantity of sodium bicarbonate present. He apparently did not decide whether the sodium bicarbonate was combined as trona or whether it represented a new species.² F. Zambonini found crystals of trona in the cavities of a leucite-tephrite at the base of the crater in the Atrio del Cavallo, Vesuvius, near the lava flow of 1895. He obtained sufficient optical and crystallographic data to decide definitely that the mineral was trona.³ He also heated about one-tenth of a gram of the material and found the loss in weight to agree closely with that to be expected for trona. F. S. Starrabba, in an account of sodium carbonate minerals from Etna,⁴ makes no mention of free sodium bicarbonate. He also gives no complete analysis for trona and he observes that the loss of weight on heating is higher than the theoretical value for trona. He attributes this to admixture with natron. It may be noted here that admixture with sodium bicarbonate would also increase the loss of weight on heating. The data on Italian trona are therefore very scanty.

Numerous analyses, however, have been published for trona from other localities. Doelter, for instance, gives in his 'Handbuch der Mineralchemie' 1912, vol. 1, part 1, pp. 186-187, a list of twenty from various places. He points out that whereas all the recent

¹ F. Stolba, Journ. Prakt. Chem., 1866, vol. 97, p. 503.

² V. R. Matteucci, Sul bicarbonato sodico prodotti sulle lave dell'eruzione vesuviana principiata il 3 luglio 1895. Rend. Accad. Sci. Fis. Mat. Napoli, 1897, ser. 3, vol. 3 (= Ann. 36), p. 223.

³ F. Zambonini, Atti Accad. Sci. Fis. Mat. Napoli, 1908, ser. 2, vol. 13, p. 38.

⁴ F. S. Starrabba, Revista Min. Crist. Ital., 1913, vol. 42, p. 51.

analyses and many of the earlier ones support Laurent's formula (1852), $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, a few agree with Klaproth's formula (1802), namely $\text{Na}_2\text{CO}_3 \cdot 2\text{NaHCO}_3 \cdot 3\text{H}_2\text{O}$. The analyses of trona from Egypt by Popp¹ made in 1870 are the only analyses of recent times which support the latter formula. Nevertheless, for some time all analyses of trona were reduced to the sesquicarbonate formula. It was Chatard² who showed in 1889 that his own analyses of trona from Owen's Lake, California, and most of the earlier analyses, except Popp's, when recalculated, supported much more satisfactorily the now generally accepted formula, namely, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$. Doelter rightly concludes that all naturally occurring trona whose composition cannot be represented by this formula must be mixtures of trona with other sodium carbonates. If we recalculate all these analyses which do not agree, we find some of them to be mixtures of trona with thermonatrite or natron, or both; but a few remain which cannot be explained in this way. Those in fact which support Klaproth's formula must be mixtures of trona, thermonatrite or natron, and free sodium bicarbonate. If the analyses of Klaproth and Popp be recalculated, using the correct formula for trona, the amount of free sodium bicarbonate present varies from 15 to 20%. Unless Klaproth and Popp were grossly inaccurate in their methods they must have been analysing a mixture containing, in addition to trona, free sodium bicarbonate. Recently, P. Walther (*loc. cit.*), whilst examining the sodium carbonate deposits of the Magadi Lakes, Kenya Colony, discovered in the salt crusts of Little Magadi, bladed crystals, harder than trona, composed of very nearly pure sodium bicarbonate. He did not obtain any physical data on these crystals and refrained with commendable caution from giving a new name. This short review of what is known about the occurrence of sodium bicarbonate in nature is, to some extent, confirmatory evidence for the existence of sodium bicarbonate as a mineral. In my opinion the physical and chemical data obtained in working on the so-called 'thermokalite' clearly prove the presence of a considerable quantity, at least 20%, of free sodium bicarbonate and justify the naming of a new mineral.

Dr. L. J. Spencer has very kindly suggested an ingenious name, *Nahcolite*. The significance of the name is appreciated when written NaHCO -lite, and it gives a useful 'memoria technica' for distinguishing

¹ O. Popp, *Ann. Chem. Pharm.*, 1870, vol. 155, p. 248.

² T. M. Chatard, *Amer. Journ. Sci.*, 1889, ser. 3, vol. 38, p. 59.

still another sodium carbonate mineral. It is unfortunate that in these crusts the nahcolite occurs in such small crystals and mixed with so many other salts. The mineral, though adequate for determinative purposes, is obviously unsuitable for crystallographic or accurate optical measurements. It is also difficult to separate sufficient from the original masses for a really reliable analysis.

In conclusion, some remarks, chiefly speculative, will be made on the genesis of nahcolite at Baia. The mode of formation of the saline crusts in the cuniculi is not definitely known. The material of which the hill is made, viz. a pumiceous tuff, has been acted upon considerably by the fumarolic gases of the Phlegrean Fields. The tuff at the surface of the tunnel was friable and quite decomposed. It is a possibility, therefore, that the saline incrustation is an efflorescence on the walls of tuff forming the cuniculus. On the other hand, the deposits equally well suggest evaporation products from the water of the hot springs. Whilst it is not certain how the 'thermokalite' was actually formed, there is more hope of discussing the conditions under which the several components of the mixture might be expected to appear. We have already dealt with the conditions of formation of two components, thenardite and thermonatrite. It was necessary to consider the high temperature and the humidity of the air of the cuniculus. In order to explain the formation and stability of nahcolite, a further constituent of the air in the cuniculus must be considered, viz. carbon dioxide. Brun's analyses of gases contained in Vesuvian lavas¹ and similar work of Shepherd and Merwin on the Mt. Pelée lavas² show how important a constituent is this gas. The Grotto del Cane, near Naples, is a famous instance of continuous evolution of carbon dioxide from the surrounding rock. The gas has also been observed bubbling up through thermal springs of this locality. The high temperature of the volcanic hill backing Baia is a favourable condition for evolution of carbon dioxide and, prior to the increased ventilation brought about by tunnelling for the Cumana railway, the Roman cuniculi must have been excellent receptacles for the gas. Even after tunnelling, we know from Dr. Johnston-Lavis's observations, there was considerable carbon dioxide inside the cuniculus. Whether, then, we regard the incrusta-

¹ A. Brun, *Recherches sur l'exhalaison volcanique*. Geneva and Paris, 1911, pp. 95-97.

² E. S. Shepherd and H. E. Merwin, *Journ. Geol. Chicago*, 1921, vol. 35, pp. 76-116. [Min. Abstr., vol. 3, p. 502.]

tions as formed by the evaporation of the hot springs containing plentiful carbon dioxide in solution, or whether we consider the action of carbon dioxide on an efflorescence coating the walls of the cuniculus, in either case the conditions must have been suitable for the formation of trona. In order to decide whether nahcolite could have been formed and maintained in a stable condition at such a temperature we ought to know whether the partial pressures of the water-vapour and carbon dioxide were sufficiently high. Although this knowledge is lacking, it is interesting to calculate the order of magnitude of the necessary pressures. Many experimenters have studied the decomposition of sodium bicarbonate, but their data vary considerably. The most reliable work of recent date is that carried out by Caven and Sand¹ on the alkali bicarbonates. One system studied carefully was :



The experimental values of the vapour-pressure (p) at various temperatures over the range 85°–110° C. agreed with the theoretical formula

$$\log p = 11.8185 - \frac{3340}{T}, \text{ where } T \text{ is the absolute temperature.}$$

At temperatures below 85° C. the results were vitiated by the formation of crusts on the surface, which greatly retard the velocity of the reaction. Days were taken, even at temperatures of about 90° C., to obtain equilibrium on raising the temperature. The authors consider that this difficulty probably accounts for the lack of agreement amongst previous experimenters. We can probably obtain a fairly accurate calculated value for p at 70° C., however, by using their formula. The vapour-pressure of the system at this temperature is roughly one-sixth of an atmosphere. Hence in order to maintain the bicarbonate in a stable condition at such a temperature the amount of carbon dioxide in the air must be at least 8 % by volume. However, there were probably at least two more components present, viz. thermonatrite and trona. The authors failed to obtain experimental values for a four-component system, but their calculations show that the partial pressure of the carbon dioxide is about 30 mm. at 70° C. It is to be noted that the necessary pressure of water-vapour, 120 mm., is much less than the vapour-pressure of natron or mirabilite at this

¹ R. M. Caven and H. J. S. Sand, Journ. Chem. Soc. London, 1911, vol. 99, pp. 1359–1369.

temperature, (viz. over 200 mm.). That is, the water-vapour necessary to maintain a system containing nahcolite and thermonatrite in equilibrium is not sufficient to form natron or mirabilite. We have no data for a system containing trona in addition, but it can be shown that the approximate value of 30 mm. for the partial pressure of carbon dioxide obtained above for the four-component system would not be materially altered. Thus, as nahcolite was found at a temperature probably higher than 70° C., the amount of carbon dioxide present in the cuculus must have been about 4 % by volume. At 90° C., however, this figure would have to be about 16 %.

Caven and Sand's work therefore enables us to make an approximate guess as to the condition of the atmosphere in the cuculus. Their work also throws light upon a further matter. It is a general opinion that sodium bicarbonate can never exist as a mineral under ordinary conditions. If it be formed then it is rapidly and completely converted into trona. Only the presence of excess carbon dioxide in the atmosphere would render it stable. Such an opinion is probably based on experiments on the decomposition of sodium bicarbonate. The work of Caven and Sand indicates the difficulty of obtaining reliable data at low temperatures owing to 'retardation'. If we make use of their formula at room temperatures we find that the partial pressure of carbon dioxide necessary to maintain the stability of nahcolite at 20° C. is of the same order as that exerted by the normal carbon dioxide content of the atmosphere, viz. 0.03 % to 0.3 % by volume. This, however, is not an experimental result. Until the decomposition pressure of sodium bicarbonate has been measured at ordinary temperatures no accurate conclusions are possible. The formation of crusts referred to by Caven and Sand is very important. At ordinary temperatures this 'retarding' factor would prevent equilibrium from being reached for a long time. Thus fluctuations in the carbon dioxide content of the atmosphere would have no effect once these crusts were formed. It is possible that even when the pressure exerted by the carbon dioxide of the atmosphere is lower than the partial pressure of the bicarbonate, decomposition after a time will be arrested and the reaction will not proceed to completion. In confirmation of this it is known that artificial sodium bicarbonate when exposed to the atmosphere gives off carbon dioxide till a certain proportion of the normal carbonate is formed, when further decomposition is only effected by leaching out the

sodium carbonate. This is, at all events, a probable explanation of the presence of at least 20% nahcolite in a saline incrustation collected about forty years ago.

In conclusion, I should like to thank the Keeper of Minerals, Dr. L. J. Spencer, for his continual assistance and helpful criticism. Without his aid the work would have been full of omissions.
