

the reaction would then be influenced by conditions dependent on the heterogeneity of the medium. It is quite futile therefore to attempt to apply to these reactions the temperature coefficients determined for homogeneous systems or for systems of differing heterogeneity.

Nor is it by any means certain that the speed of biological processes is controlled by the speed of some one or more chemical reactions. In his attempt to answer the question Kanitz points out that a number of physical factors have exactly the temperature coefficient of chemical reactions. To the list cited by Kanitz¹⁰ it may be well to add a process which is perhaps of great importance for biological activities. It has been shown that some coagulative processes have the temperature coefficient of a chemical reaction.¹¹

The recent determination of the temperature curve of protoplasmic viscosity¹² may be of use in deciding the question as to whether the speed of living processes is controlled by chemical or physical forces. In some cells at least, as the temperature rises to 15° the viscosity increases. With further increase in temperature there is for a time a decrease in viscosity. If the speed of protoplasmic activity in general were controlled by one or more chemical reactions we would expect that the temperature coefficient of this reaction or reactions would be less below 15° than above 15°.¹³ In many instances this is exactly the opposite of the truth. It has often been shown that the temperature coefficient of many biological processes is greater below 15° than above 15°. Kanitz¹⁴ cites numerous cases, the phenomenon was emphasized by Mlle. Filon,¹⁵ who quotes earlier references, and within the last year it has once more been elaborately emphasized by Crozier. But this argument does not settle the question. It could be supposed, as Pütter does, that as the temperature is raised, at some critical point a reaction with lower temperature coefficient may become the slowest reaction and take the place of the reaction with higher temperature coefficient which previously held this position. Such an explanation would not hold for those cases in which the tem-

perature coefficient increases at a critical point. Cases of this sort apparently occur, as Pütter points out. But even so it might be possible to explain all types of cases on a purely chemical basis if we care to assume with Pütter that the speed of biological processes may to some extent be determined by chemical reactions which tend to retard the biological process.

It is rather astonishing to find Crozier¹⁶ using the Blackmann-Pütter concept to explain cases in which as the temperature rises past a critical point, the controlling reaction is shifted from one with a relatively low temperature coefficient to one with a relatively high temperature coefficient. As the temperature rises we would have the reaction with relatively high temperature coefficient growing increasingly more rapid than the reaction with relatively low temperature coefficient. Crozier assumes that it may become slower. This is evidently a contradiction in terms. There are also other surprising deductions in Crozier's papers. Again and again he advances the hypothesis that oxidations and other biological processes are controlled by reactions in which H or OH ions are the sole catalysts. Such a hypothesis does not fit in very well with the prevailing notion that enzymes play at least some part in practically all biological reactions.

Finally it may be well to again sound the note of caution so frequently voiced by older students of temperature coefficients. The problem is far from simple, it is highly complex. The determination of the temperature coefficient of the entire ensemble of more or less unrelated chemical and physical phenomena involved in the movement of an ant or the duration of life of an insect larva, the comparison of this average temperature coefficient with the temperature coefficient of a single chemical reaction occurring in a totally different sort of a medium, may be interesting as a mathematical exercise, but it can hardly be assumed that any information so gained or that any immediate development of these widely-used methods of attack "may lead to an extremely important method of identifying reactions in undisturbed living matter."¹⁷

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SPECIAL ARTICLES

A NEW SOURCE OF POSITIVE IONS

IN researches with positive ions, considerable difficulty has been met in obtaining a satisfactory source of the required ions. Actually, there has been no source of positive ions which can compare to the present source of electrons in regard to constancy and ease of control.

¹⁶ Crozier, *l.c.*

¹⁷ Crozier, 1924, *Jour. Gen. Physiol.*, VII, 189.

¹⁰ Kanitz, 1915, "Temperatur und Lebensvorgänge," Berlin.

¹¹ See Freundlich, *l.c.*, p. 640.

¹² Heilbrunn, 1924, *Amer. Jour. Physiol.*, LXVIII, 645.

¹³ For as the temperature rises to 15° the viscosity increase would tend to slow the reaction and as the temperature rises above 15° the viscosity decrease would tend to hasten it. But it must be remembered that the viscosity changes in protoplasm may involve only the grosser elements and that such changes might have little effect on the velocity of chemical reactions.

¹⁴ Kanitz, *l.c.*

¹⁵ Filon, 1911, *Jour. de physiol. et de path. gen.*, XIII, 19.

Two sources of positive ions have been generally used to date: (1) The positive ions given off by heated metals, salts, or coated surfaces;¹ and (2) the positive ions or anode rays given off from a cold or hot anode, under electron or cathode ray bombardment.² In the case of the hot surfaces, the initial values of the positive emission were relatively high and decreased with time. The positive emission was a mixture of metallic ions and depended upon the presence of gas and previous gas treatment of the substance. In the anode rays, the variation in the discharge and temperature of the anode was always accompanied by a similar variation in the positive ion current, or anode rays.

In a thermionic investigation of the catalysts used for the synthesis of ammonia at the Fixed Nitrogen Research Laboratory, it was discovered that certain catalysts gave a copious and a very steady supply of positive ions. Positive ion currents as large as 10^{-4} amperes per square centimeter were observed. The emission was so constant at a given temperature that definite values of Richardson's work function could be obtained for these positive ions from the hot surface.

It has been found that either the catalyst granules themselves could be used as the hot anode, or the powdered catalysts could be coated on a platinum ribbon and used as the hot anode. The material consisted of a previously well fused mixture of iron oxide and about 1 per cent. of an oxide of an alkali or alkaline earth metal and in some cases also contained about 1 per cent. aluminum oxide. These mixtures are referred to as promoted catalyst. The iron is usually considered the catalyst proper and the other constituents are the promoters. The fusion had been carried out in a bed of the same material between water-cooled iron electrodes.³ The mixture could be either partially reduced in an atmosphere of hydrogen at about 400° C. before being installed as the anode, or the unreduced material could be mounted as the anode and partially reduced in place. After a preliminary heat treatment which consisted of degassing and glowing the material, the positive ion current was very steady at a given temperature in a vacuum of 10^{-6} mm of Hg. By varying the temperature through several hundred degrees within the range of 400° to 1070° C., depending on the material

studied, it was found that the positive current obeyed Richardson's equation $I_+ = AT^{\frac{1}{2}} e^{-\frac{b}{T}}$ where $b = \frac{\phi e}{k}$.

Where I_+ is the saturation current, A and b constants of the equation, ϕ is the equivalent work function in volts, e the unit electric charge, k the Boltzmann gas constant, and T the absolute temperature. From this equation definite values of ϕ_+ for the positive ions were obtained from a fused mixture containing potassium.⁴ From observations on the electron emission characteristics of a tungsten filament, placed so as to collect ionized vapor coming from the hot surface, it was concluded that the positive current consisted of positively charged atoms of potassium. Very recently, H. A. Barton at Princeton, through the courtesy of Professor K. T. Compton, tested this material in a mass spectrograph. The results showed very conclusively that the positively charged particles were singly charged atoms of potassium and that no other charged particles were emitted.

A sample from a thoroughly fused mixture of the oxides of iron, aluminum and caesium was also investigated and found to be a very suitable source of positively charged caesium ions. Other investigations on fusions of the oxides of iron, aluminum and an alkaline earth metal show that these mixtures also are good sources of positive ions. We believe the ions here observed are positive ions of the alkaline earth metal which had been introduced in the original mixture. It is hoped that the mass spectrograph results for these mixtures will show this as conclusively as they did in the case of potassium.

The lowest temperature at which the positive emission could be detected depended upon the mixture. This temperature was the lowest for mixtures containing caesium and the highest for mixtures containing an alkaline earth metal.

There now exists therefore a source of positive ions of the alkali metals and no doubt alkaline earth metals which compare in constancy, ease of operation and control, with the present thermionic sources of electrons.

A new field of research should be opened up by this high vacuum source of positive ions. Experiments on ionization effects in gases and on surfaces with this source of positive ions, together with the possible influence of the positive emission from the catalyst surface on catalytic activity, are under investigation.

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⁴ Kunsman, *Phys. Rev.*, 25, 892, June, 1925.

¹ O. W. Richardson, "Emission of Electricity from Hot Bodies," 2nd ed., chap. 6-8.

² Dempster, *Phys. Rev.*, 11, 316 (1918); 18, 415 (1921); Aston, *Phil. Mag.*, 42, 436 (1921).

³ Method of preparation to be described by Larson and Richardson in the *Journal of Industrial and Engineering Chemistry*.