

Some weeks later at the Chicago meeting of the National Academy of Sciences, during the discussion of a paper, I commented on Dr. Denham's statements, and pointed out that this study had added cobalt to the known "essential" elements. Much to my chagrin these statements were distorted in press reports of the academy meetings, and I and my laboratories at Minnesota were credited with this discovery. In so far as I could, I attempted to correct the false report, for we have made no studies of this sort at Minnesota. Nevertheless we were given the credit in the "Summary of Science for 1936" in the columns of one of the New York daily newspapers. Accordingly, I wrote Dr. Denham and asked him to prepare a short statement outlining the scope of the work and the essential findings which could be submitted for publication in the United States in order that credit may be given where credit is due. Dr. Denham's statement, submitted in response to my request, follows.

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COBALT INVESTIGATIONS IN NEW ZEALAND

In the course of the Liversidge Lecture delivered at the recent bi-annual meeting of the Australia and New Zealand Association for the Advancement of Science by Mr. T. Rigg, director of the Cawthron Institute, the progress of the cooperative investigations of the Department of Scientific and Industrial Research of New Zealand and the Cawthron Institute in regard to cobalt deficiency in New Zealand was reviewed.

Mr. Rigg stated that at both Morton Mains, Southland, and Glenhope, Nelson, the use of cobalt drenches supplying 8 mg cobalt per week had been completely effective in preventing and in curing sheep ailment. Furthermore, in both localities the curative properties of drench materials, which in former years had given success in the treatment of stock ailment, had been shown to be dependent not on their iron content but on a relatively high content of cobalt. Nelson soil used with success in earlier experiments at both Morton Mains and Glenhope contained 56 parts per million of cobalt. Whangarei limonite (Reyburn's), which had been shown by B. C. Aston to be so beneficial in controlling "bushsickness" on the pumice soils of the North Island, contained likewise approximately 60 parts per million of cobalt. Other drench materials, which have not proved successful in the control of stock ailment of the bushsickness type, contained relatively little cobalt. At both Glenhope and Morton Mains, acid extracts of beneficial drench materials, carefully freed from iron, gave the same results as pure cobalt salts. Recent experiments of the chemistry department of the Department of Agriculture of New

Zealand had likewise shown, in the case of typical bushsickness of the North Island, that carefully purified ferric ammonium citrate was non-effective in the control of bushsickness and that cobalt salts were highly beneficial.

Much work is now in progress to determine whether there is an actual deficiency of cobalt in the pastures, soils and animal organs of the areas affected with stock ailment. Investigations are not complete, but substantial evidence is being obtained of a low cobalt status associated with affected areas. Askew and Dixon in a paper presented at the same meeting and dealing with the cobalt status of animal organs at Glenhope and Morton Mains showed conclusively that the liver, pancreas and blood of affected sheep contained very much less cobalt than corresponding organs from healthy sheep. Frequently the amount of cobalt was one tenth in the case of livers of that associated with healthy sheep, *e.g.*, cobalt content of healthy livers 0.15 to 0.25 p.p.m. compared with 0.02 p.p.m. for affected sheep. The cobalt content of livers taken from sheep drenched with cobalt salts was approximately 0.20 p.p.m. on the dry basis, corresponding closely to the cobalt content of livers from healthy sheep killed at the freezing works.

Determinations of cobalt in pastures have not proceeded far enough to enable the position to be summarized, but in the case of Glenhope pasture there is every indication that the cobalt content of affected pastures is considerably lower than that of adjoining healthy pastures. One interesting feature of the pastures investigations is the rapid intake of cobalt by pasture plants, demonstrating the possibility of using small top-dressings of soluble cobalt salts in the treatment of affected pastures. The cobalt survey of New Zealand soils made by Miss E. B. Kidson in the main has confirmed a low cobalt status of soils in association with stock ailment. One or two soils, however, gave anomalous results. These results could possibly be explained on an assumption of difference in "availability," but so far attempts to determine available cobalt in soils have not proved successful. The soil results indicate that a low cobalt status of the soil is not always a satisfactory index of the need for cobalt supplements for stock.

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THERMODYNAMICS AND THE RATES OF COUPLED OR REVERSED REACTIONS

THERMODYNAMICS can give us more valuable information concerning reaction velocities than is often suspected. It is of course true that with thermody-

namics alone it is impossible to obtain even an estimate of the absolute magnitude of a reaction velocity. This apparent weakness, due to the very nature of thermodynamics, is actually a power, since it enables us to establish theorems on reaction rates which are independent of the magnitude of these rates and of the intimate reaction mechanisms. The situation is indeed quite similar with most of the other physical or chemical quantities with which thermodynamics is concerned.

A particularly simple and fruitful way of expressing the criterion for irreversible changes given by the second law of thermodynamics is to state that in the case of one single irreversible reaction, the product of affinity and reaction velocity is necessarily positive¹:

$$A v > 0 \quad (1)$$

The velocity v is the time derivative of the degree of advancement of the reaction, the affinity A is defined, for instance, as minus the partial derivative of the free energy or thermodynamic potential with respect to this degree of advancement, pressure and temperature being constant. If two independent reactions occur simultaneously in the system, the second law requires

$$A_1 v_1 + A_2 v_2 > 0 \quad (2)$$

Two reactions are independent when, representing them by ordinary chemical formulas, it is impossible to derive one from the other by some rearrangement. Several reactions are independent when none of them can be derived from the others by means of a linear combination. Suppose now that, for some particular state of the system, we have $A_2 > 0$, $v_2 > 0$, $A_1 < 0$.

It follows from (2) that

$$v_1 < -\frac{A_2}{A_1} v_2 \quad (3)$$

(Division by $A_1 < 0$ requires the change in the sign of the inequality). This upper limit of v_1 is positive, which shows that reaction 1 may occur in its unnatural direction. In other words, coupling of reaction 1 by reaction 2 is thermodynamically possible. The velocity of the coupled reaction must, however, remain inferior to a certain definite limit. We should add that the equality sign is also allowed in formula (3). We consider this very simple theorem as a typical piece of thermodynamic information concerning reaction rates.

Coupled or reversed reactions in biological systems have been observed and discussed by Borsook² and

other authors. We hope that rate measurements will at some time or other be made on such systems and that our formula (3) will then be directly verified. We would also be interested in discovering a clear-cut case of coupling in some non-biological system.

A more detailed study of the thermodynamics of coupled reactions has been published elsewhere.³

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MAGNIFICATION OF TIME AS A RESEARCH TECHNIQUE IN THE STUDY OF BEHAVIOR

THE magnification or condensation of *space* by means of a microscope or telescope and the magnification or condensation of *energy* through thousands of mechanical and electrical devices are established scientific methods which we take for granted. It seems peculiar that the magnification or condensation of *time* has so infrequently entered into scientific concept and methodology, particularly since the means of such time magnification or condensation have been at hand and used for twenty or thirty years. We refer to ultra-rapid and infra-slow motion picture photography.

Ultra-rapid motion picture photography usually refers to pictures taken at approximately 64 exposures per second and subsequently projected at 16 to 20 exposures per second, thus affording a time magnification of four. Until recently comparatively little work has been done above this speed. The problems of film sensitivity, shutter speed, intermittent forward motion of film and of high illumination have all been obstacles. With the perfection of the revolving prism camera by Day, of stroboscopic illumination and synchronized camera by Edgerton, and of the commercial production of supersensitive film, we now have facilities for the magnification of time to effects which are higher than 200 "diameters."

As an example of the application of these new time magnification methods we have been making a study of the behavior responses of adults, infants, children and the higher primates to the sound of a pistol shot. To the naked eye this response is a confused mass of behavior. Using cameras running at a speed of 64 exposures per second it has been possible to demonstrate a clear, unmistakable, immediate, stable, reflex pattern in all the groups we have studied. This primary pattern is very rapid and is usually complete in one-half second or less. The primary response is then followed by a secondary response which is variable, differs among individuals and partakes of the nature of a socialized, conventional, learned response

¹ Th. De Donder and P. Van Rysselberghe, "Thermodynamic Theory of Affinity. A Book of Principles," Stanford University Press, 1936. P. Van Rysselberghe: *Chemical Reviews*, 16: 37, 1935.

² H. F. Schott and H. Borsook, *SCIENCE*, 77: 589, 1933; H. Borsook, *Ergebnisse d. Enzymforschung*, 4: 1, 1935, etc.

³ P. Van Rysselberghe, Académie royale de Belgique, *Bulletins de la Classe des Sciences*, December, 1936.