

Fig. 1. Crystalline rhodanese from ammonium sulfate, pH 7.8. × 308.

pH 7.8 as small, strongly lightdispersing cubes or larger rectangular plates, see Fig. 1. The specific activity of the preparation was raised from 0.84 to 1.0 by crystallisation, the crystalline enzyme being purified 650-fold from the starting material.

1  $\mu$ g of crystalline rhodanese was able to form 2.84  $\mu$ -equivalents of thiocyanate during 5 minutes incubation at 20° C. Assuming the molecular weight of the enzyme = 35 000 this corresponds to a turnover number of 20 000 min<sup>-1</sup>. Our test system was of pH 8.75 and contained in a final volume of 2.5 ml 0.1 M thiosulfate, 0.05 M cyanide, 0.08 M phosphate and 0.125 mg bovine albumin. The albumin was found to be necessary in order to obtain full activity with the more purified enzyme preparations.

The crystalline enzyme gave a colorless solution with an ordinary protein absorption spectrum, which was not changed by the presence of  $0.05\ M$  thiosulfate at pH 7.4. No formation of an enzyme-substrate compound could thus be observed spectrophotometrically.

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A detailed report will be published in a near future.

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## On the Principle of Thermal Interaction

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In a recent work Holtan 1 states a principle of thermal interaction: "In a non-isothermal process there is an interaction between the flow of heat and the transport phenomena in such a way that the loss of work (loss of potential energy) for the transport of entropy bound to chemical substance can be compensated partly or completely by the transport of free entropy contained in the flow of heat in the opposite direction."

This principle is embodied in the principle of least dissipation of energy. It is thus possible to prove the principle of thermal interaction for the cases where the principle of least dissipation of energy is valid. The restrictions and variations with respect to which the dissipation is a minimum, are stated by Wergeland <sup>2</sup>.

For a process under consideration we can split the total rate of increase  $\dot{S}$  in the entropy of the system in two parts:

$$\dot{S} = 2\Phi - \dot{S} *$$

In the stationary state  $\hat{S}$  will be zero, and the dissipation function  $\Phi$  can be shown to be a minimum. Consequently the total flow of entropy across the surface of the system,  $\hat{S}^*$ , will be a minimum.

This flow is given by the following expression (see for instance 3):

$$\dot{S}^* = \int_F (\overrightarrow{J_u} - \sum \frac{\mu_i \overrightarrow{J_i}}{T}) \, dF$$

 $J_i$  is the flow,  $\mu_i$  is the chemical potential of the i'th species of particles, and  $J_u$  is the flow of internal energy. F is the surface of the system.

If we now write, considering a one component system:

$$\overrightarrow{J_i} = \overrightarrow{J}, \mu_i = h - Ts$$

$$\overrightarrow{J_u} = \overrightarrow{q} + h\overrightarrow{J}$$

and

where q is the pure heat flow, we have:

$$\dot{S}^* = \int_{F} \frac{q}{(T + sJ)} \, dF$$

If this integration is performed on the interface between two systems which, except for this interface, are isolated, we arrive at the following requirement:

 $S_t' + S_b' = \text{minimum},$ where  $S_f' = \int_F \frac{q}{T} \frac{dF}{dF}$  is the entropy transport due to the pure heat flow and  $S'_b = \int_F \stackrel{\rightarrow}{sJ} dF$  is the entropy transport bound to the chemical substance. We therefore have:

$$\delta S_f' = -\delta S_b'$$

so that in the stationary case the two entropy flows tend to compensate each other. the compensation being complete in the reversible case where the dissipation is zero. This is exactly the principle of thermal interaction.

- 1. Holtan jr, H. J. Chem. Phys. 19 (1952) 519.
- 2. Wergeland, H. Kgl. Norske Videnskab. Selskabs Forh. 24 (1951) No. 25. 3. Meixner, J. Ann. Physik 39 (1941) 333.

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