the catalytic effect was observed in adsorption on a non-specific macromolecular non-protein carrier. The test system simulates a biocatalyst in which the active group is weakly bound to the remainder of the enzyme.

The experiments were performed in water and in organic solvents which contained hardly any oxygen (less than 0.02%); they were carried out both under static conditions and in a flow system.
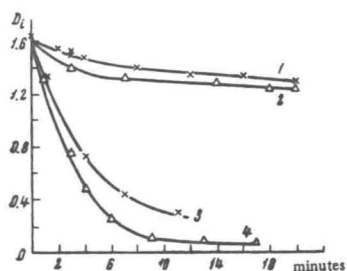

Figure 1.

Hydrogen sulphide is known to be slowly oxidised by atmospheric oxygen. The oxidation is accelerated in the presence of reversibly reduced dyes—agents for hydrogen transfer from hydrogen sulphide to oxygen. We investigated the effect of adsorbed dyes on the oxidation of hydrogen sulphide. Since the experimental solutions contained no oxygen, the dyes having combined with hydrogen were converted into their colourless leuco-forms and remained in this state. Consequently, the reaction could be followed by the decrease in the intensity of the colour. We found the pH range in which the rate of reduction of dyes is a maximum: pH 2.5–5 for Methylene Blue and pH 4–5 for Indigo Carmine.
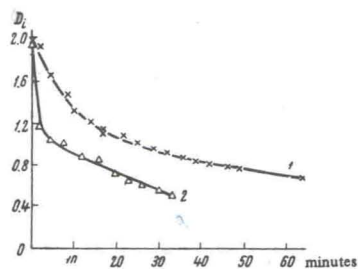

Figure 2.

Fig. 1 (for Methylene Blue) and Fig. 2 (for Indigo Carmine) present the curves for the interaction of the dyes with hydrogen sulphide. It is evident that the decrease of the optical densities of the dye solutions in the presence of cellulose (curves 2 and 4) is much faster. This indicates an enhancement of the catalytic effect of the dye adsorbed on cellulose. Methylene Blue is more readily reduced in an acid medium.

In the adsorption of Methylene Blue on cellulose the formation of its "red form" was observed. The optical spectra of the "red form" of Methylene Blue in various solvents differ sharply from those of the usual form of the dye in the same solvents. The "red form" is soluble in carbon tetrachloride, 1,2-dichloroethane, dioxan, absolute ethanol, and acetone, and in all these solvents its spectra have absorption maxima at 496, 534, 513, 541, and 548 nm respectively. The rates of reduction of the "red" and "blue" forms of Methylene Blue were compared in absolute ethanol and acetone. It was found that in both solvents the "red form" is reduced with greater difficulty.

In adsorption on cellulose only a small part of Methylene Blue is converted into the "red form". The formation of the "red form" confirms the hypothesis that the dye enters into a close interaction with cellulose. This leads to the formation of various forms of the adsorbed dye up to the chemically altered (compared with the normal dye) "red form" of Methylene Blue.

Both Methylene Blue and Indigo Carmine have ESR spectra which change on addition of hydrogen sulphide. The ESR spectrum of the "red form" differs from that of the usual form of Methylene Blue, and they change in different ways on addition of hydrogen sulphide. Studies on the changes in the ESR spectra of dyes during the reactions constitute reliable evidence of the radical nature of the process involving the conversion of the dyes into the leuco-forms under the action of hydrogen sulphide.

The complete paper is deposited at the All-Union Institute of Scientific and Technical Information (VINITI) (No. 419-68, from 31st December, 1968).

Thermostatic Control of High-pressure Vessels in Physicochemical Studies

V.F.Fadeev

An automatic method of temperature control distinguished by simplicity of construction and the capacity to maintain a constant temperature in the thermostat to a high degree of accuracy is considered in this paper. High-pressure vessels usually have very thick walls, which constitute a kind of thermal resistance. Therefore, if the temperature of the vessel walls is maintained to within 0.05 deg, for example, the solution of the thermal conductivity equation for this case shows that the temperature within the vessel will undergo oscillations smaller by a factor of about 25 (when the ratio of the external and internal radii of the vessel is 12 and the thermal diffusivity of steel is about 0.17 cm^2 s^{-1}). Thus when high-pressure vessels are thermostatted, the requirements for the precision of temperature control may not be very rigorous.

The proposed control system has a wide range of adjustment and is independent of the inertia of the thermostat. The equation for the system controlled is as follows:

$$P = \frac{\lambda ST}{h} + c \frac{dT}{d\tau},\qquad(1)$$

where P is the power produced by the heater, T and c are the temperature of the thermostat liquid and its heat capacity, h and λ are the thickness of the thermostat walls and