

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.

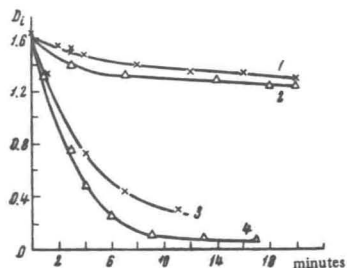


Figure 1.

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.

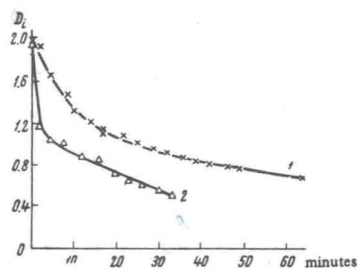


Figure 2.

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).

Moscow Institute
of Railway
Transport
Engineering

Received 30th September 1968

U. D. C. 541/.543 : 539.893

Thermostatic Control of High-pressure Vessels in Physicochemical Studies

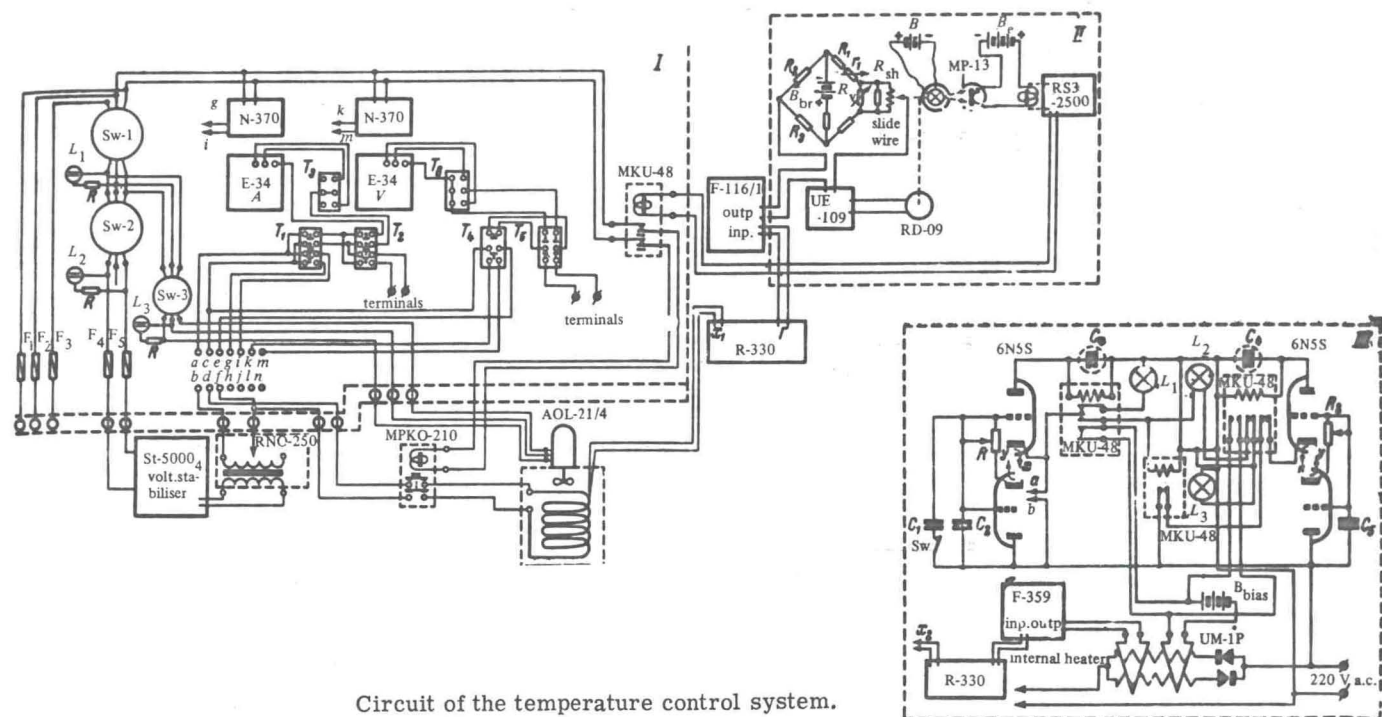
V.F. Fadeev

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 $0.17 \text{ cm}^2 \text{ s}^{-1}$). 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:

$$P = \frac{\lambda \Delta T}{h} + c \frac{dT}{dt}, \quad (1)$$

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



Circuit of the temperature control system.

their thermal diffusivity, S is the area of the outer surface of the thermostat, and τ the time.

Under regular conditions, the temperature changes according to the law

$$T = C_1 \exp\left(-\frac{\lambda S}{ch} \tau\right) a \cos \omega \tau + b \sin \omega \tau, \quad (2)$$

$$a = -P/c[1 + (\lambda S/ch)^2]; \quad b = P\lambda S/c^2 h[1 + (\lambda S/ch)^2];$$

when $\tau \rightarrow \infty$, the first term may be neglected. The period during which the heater must be switched on to give minimum temperature variation in the thermostat can be readily found from Eqn. (2). In the present case for $\lambda = 0.013$ kcal m⁻¹ deg⁻¹ min⁻¹, $c = 0.3$ kcal kg⁻¹ deg⁻¹ (liquid polyethylsiloxan), $S/h = 10.32$ m, and a mixture weighing 56 kg, the period is 4 min.

The circuit presented in the Figure was used for temperature control. The signal from the thermocouple was transmitted to an R-330 potentiometer, the deviations from the specified value being amplified by an F-116/1 photo-amplifier. The amplified signal is transmitted simultaneously to a potentiometric bridge and an amplifier of type UE-109. The UE-109 amplifier incorporates a synchronous motor of type RD-09, which moves the sliding contact of the potentiometric bridge slide wire compensating the error signal. A small lamp mounted on the sliding contact triggers off a photo-relay at the instant of compensation of the error signal, and the photo-relay switches on the thermostat heater. The precision of temperature control is ± 0.025 deg. The circuit of an EPP-09 potentiometer may be used in the construction of the regulator (block II in the Figure). To improve the precision of temperature control, it is possible to employ a low-power internal heater located directly on the high-pressure vessel. The internal heater must be switched on at the instant when the negative half-period of

the thermal wave reaches the surface of the high-pressure vessel. Since the parameters and dimensions of the thermostat are constant, the period between the instant of switching on the thermostat heater and the arrival of the negative thermal wave can be readily determined with the aid of an additional thermocouple. The author suggests that the internal heater be switched on with the aid of a time relay (III in the Figure) based on two 6N5S valves. At the instant when the external heater is switched on, the contacts a and b of the time relay are closed and the time count is begun. After the required period, the relay switches on the internal heater, the duration of the operation of which is limited by the second half of the time relay. Thus the decrease of temperature on the surface of the high-pressure vessel is compensated by the required (as regards duration and magnitude) power output of the internal heater. The precision of the temperature control of the high-pressure vessel can reach ± 0.01 deg.

The author thanks Candidate of Geological and Mineralogical Sciences S. M. Stishov for supervision and for making it possible to develop the above technique and also V. A. Ivanov for assistance.

The complete article is deposited at the All-Union Institute of Scientific and Technical Information (VINITI) (No. 422-68, from 31st December, 1968).

Institute of
Crystallography,
USSR Academy
of Sciences,
Moscow

Received 30th September 1968