

A MEASURING SYSTEM FOR SIMULTANEOUS MEASUREMENT OF LOCAL TEMPERATURE AND CONCENTRATION IN NONIDEAL STIRRED REACTOR

V. VESELÝ, V. VÁCLAVEK and B. PEŠAN

*Department of Chemical Engineering,
Institute of Chemical Technology, Prague 6*

Received October 5th, 1971

A measuring device for simultaneous measurement of temperature and concentration fluctuations in a nonideal stirred reactor is described. Temperature was measured by a thermistor and concentration was determined by the conductometric method. The arrangement permitted to locate a combination probe, which measured both these quantities, at any place inside the reactor. In the case of a simultaneous measurement of several quantities the data indicated that it is important that a dynamic balance of all measuring channels be ensured. The hydrolysis of acetanhydride was used as a model reaction. The method of simultaneous measurement can be used to study nonideal mixing and to solve other problems of chemical reaction engineering.

Measurement of different scalar and vector quantities in a turbulent field is of both theoretical and practical importance. Measurement of pressure, temperature, concentration, velocity and other properties of flowing liquids can serve as examples. This paper deals with the design of a probe and a measuring system for simultaneous local measurements of concentration and temperature inside a stirred vessel in which a chemical reaction is taking place.

Existence of temperature and concentration gradients is typical of the nonideal continuous flow stirred tank reactor (CFSTR), especially in the reaction zone between the feeds and the mixer. We took our measurements in a reactor of this type. Temperature belongs among the quantities which can easier be measured than *e.g.* concentration. Therefore, the simultaneous local measurement of the temperature and concentration profiles in the CFSTR could also yield information on how to evaluate the concentration profiles without performing their direct, more difficult measurement.

Several authors published articles on the measurement or concentration fluctuations in the turbulent field. A survey of the literature data can be found in the paper by Torrest and Ranz¹. It follows that for electrolytes the conductivity method still hold its importance in comparison with more modern optical methods, although in this case the flow is distorted by the probe. It can also be seen that during the last 10–15 years an effort was exerted for miniaturization of the probe and improvement of its dynamic properties. Prausnitz and Wilhelm² described the measurement of concentration fluctuations in a packed bed. The conductivity probe sampled the volume of 10^{-3} ml. Cairnus and Prausnitz³ measured the longitudinal eddy diffusivities

in a fluidized bed by a probe of approximately the same size as that mentioned². The probe of Lamb, Manning and Wilhelm⁴ sampled a volume of $3 \cdot 10^{-5}$ ml. This progress was reached by the fact that electrodes were designed with different sizes of surface area. The indicated measured values are dominantly determined by phenomena occurring in the vicinity of the small electrode. With this probe Manning and Wilhelm⁵ carried out measurements of concentration fluctuations in a stirred, baffled vessel. Gibson and Schwarz⁶ constructed an even smaller probe, sampling a volume of $2 \cdot 10^{-7}$ ml. The tip of the small electrode was specially arranged and the large electrode was completely removed from the vicinity of the small electrode. With this probe the universal equilibrium spectra in the turbulent field behind the grid were measured. The authors also developed an interesting theoretical model for the determination of the sampled volume by a conductivity probe. Further miniaturization of the conductivity probe was made by Keeler, Petersen, Prausnitz⁷ and Torrest, Ranz¹ (volume of $5 \cdot 10^{-7}$ ml).

The magnitude of the volume controlled by the conductivity probe is not a unique characteristic of the measuring system. Other parameters exist which of course are related to the aforementioned characteristic; these are, *e.g.*, the "cell constant"⁶ the signal-to-noise ratio, the root mean square to average concentration ratio, *etc.* The problem of compensation of the temperature influence on the concentration measurement by the means of the conductivity method is discussed in the paper by Kathe, Breier and Gatzmanga⁸.

From all the papers concerning the measurement of temperature fluctuations in the liquid phase, we shall pay attention only to those dealing with measurements in a stirred reactor. Václavek and Fiedler⁹ used a standard bulb thermometer to measure the temperature profile in the adiabatic CFSTR in which an exothermic reaction of formaldehyde with ammonia took place. In this case the fluctuations of temperature in the reaction zone were found as well. Václavek, Vesely and Kořik¹⁰ measured the temperature profile in the adiabatic CFSTR by the means of a thermistor probe for 3 exothermic reactions. Worrell and Eagleton¹¹ took measurements of temperature in the adiabatic CFSTR for the determination of conversion of the exothermic reaction of thiosulphate with peroxide.

We did not find any published data on simultaneous local measurement of temperature and concentration. It appears to be promising to combine the conductivity and the thermistor methods for this purpose. However, the drawbacks immediately of this approach are also immediately evident. In addition to the fact that the conductivity of electrolytes depends on temperature, the choice of the model reaction encounters many limitations. It has to be taken into account that only one component in the reaction mixture can be conductive. In an ideal case it ought to be just that single component, the concentration

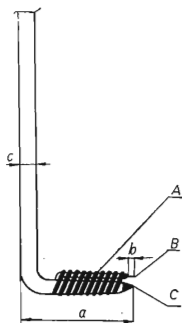
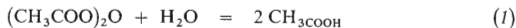


FIG. 1

The Combination Probe

A Large electrode, B small electrode, C thermistor; a 30 mm, b 1 mm, c 6 mm.

of which determines the reaction rate at a given temperature. Having eliminated several possibilities, we decided for the model reaction



for which it holds that $r_A = 51.22 \exp(-36.90/T) c_A c_B$, (gmol/l s^2), the heat of this exothermic, irreversible reaction being equal to $\Delta H = -9.98 \text{ kcal/gmol}_A$. In spite of the fact that the reaction is not quite ideal it proved to be satisfactory, and the measuring device was designed with respect to this reaction.

Construction of the Probe

The most important requirements for the probe design can be summed up as follows: The probe should be as small as possible. This permits to minimize the distortion of the flow pattern and to obtain better dynamic properties of the total measuring channel. It is necessary to eliminate errors due to electrode polarization, Joules heat, the flow of liquid around the probe, *etc.* The probe should be fixed in a device which permits to fix the probe quickly in any position inside the reactor, including the region under the mixer. In addition to these self-evident requirements which should also be respected in the case of separate measurements, it appears important that the "dynamic balance" of the measuring channels be ensured in case of more quantities being measured simultaneously. This problem will be discussed further on. A 10 NR 15 type thermistor with an exponential response was used as sensor in the temperature measurement. The semiconductor element was constituted by a pellet of 0.5 mm in diameter, sealed inside a glass jacket with an external diameter of 1 mm. The resistance of the thermistor was about 600 Ω at 20°C. The original glass tube of this standard thermistor was shortened and used for the construction of the probe (Fig. 1). The electrodes of that part of the probe which was to perform the measurement of conductivity were made of Pt wire 0.5 mm in diameter. The shape of both electrodes is shown in Fig. 1. The tip of the small electrode was about 1 mm long, and was located just beside the pellet of the thermistor. The remaining part of this wire led into the glass tube. The large electrode was formed by a coil of wire (around the glass tube near the small electrode) and the thermistor pellet. The wire of this electrode was 120 mm long. Both the electrodes were provided by Pt black in order to eliminate the effect of polarization. The probe was attached to a tube of an outside diameter of 6 mm, bent near its end at 90° so that the horizontal length of the probe was 30 mm. It can easily be shown that a probe fixed in this manner can reach any place inside the reactor, provided that $d/D = 1/3$. An approximate estimate of the volume sampled by the conductivity probe is provided by the equation

$$I = \int_s J \cdot dS. \quad (2)$$

If this electrode is taken for a sphere of radius r_1 and the sampled volume is expressed as a sphere of radius r_2 , then it holds that.

$$I = 4\pi r_1^2 J_1 = 4\pi r_2^2 J_2. \quad (3)$$

The determination of the sampled volume V_2 for a chosen decay P of current density, expressed by

$$P = J_2/J_1, \quad (4)$$

follows from Eqs (3) and (4):

$$V_2 = (r_2^3/r_1^3) V_1 = P^{-3/2} V_1 . \quad (5)$$

If the volume of the small electrode is about $2 \cdot 10^{-4} \text{ cm}^2$ and $P = 0.1$, then $V_2 \approx 6.3 \cdot 10^{-3} \text{ ml}$. This sampled volume is considerably greater in comparison with volumes achieved by other authors who have tried in the first place to miniaturize their conductivity probes as much as possible. But it must be emphasized that in the simultaneous measurement the dynamic balance is the limiting aspect of probe design. The cell constant of the probe was found to be $K = 2.8 \Omega^{-1}$.

Balance of the Dynamics Characteristics of the Two Measuring Channels

The problem of dynamics errors of the measuring system requires consideration of the local fluctuations of temperature and conductivity with time. Let the recorded output signal of conductivity from the measuring system and the output temperature signal be designated as $\lambda_0(t)$ and $T_0(t)$, respectively. The corresponding input signals are designated as $\lambda_i(t \leq 0) = 0$, $\lambda(t > 0) \neq 0$ and $T_i(t < 0) = 0$, $T_i(t > 0) \neq 0$. For the ratio of both input signals it holds that

$$\lambda_i(t) = F_i(t) T_i(t) , \quad t > 0 . \quad (6)$$

If both measuring channels are linear, with transfer characteristics $f_\lambda(t)$ and $f_T(t)$, then both the input and the output signals are related through the convolution integral

$$\lambda_0(t) = \int_0^t f_\lambda(t - \tau) \lambda_i(\tau) d\tau \quad \text{and} \quad T_0(t) = \int_0^t f_T(t - \tau) T_i(\tau) d\tau . \quad (7), (8)$$

For the output ratio $F_0(t)$ it can be written that

$$\lambda_0(t) = F_0(t) T_0(t) \quad (9)$$

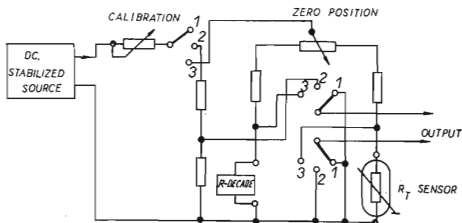


FIG. 2

The Circuit for Temperature Measurement

1 Switched off, 2 calibration, 3 measurement.

and we can obtain the following relation:

$$F_0(t) = \int_0^t f_\lambda(t - \tau) F_i(\tau) T_i(\tau) d\tau / \left(\int_0^t f_T(t - \tau) T_i(\tau) d\tau \right). \quad (10)$$

The Eq. (10) permits to assess the dynamic error of measurement. Let us consider the special case of

$$F_i(t) = \text{const.} \quad (11)$$

As it is also required that

$$F_0(t) = \text{const.} \quad (12)$$

it is sufficient to provide for a dynamic balance of both the channels *i.e.* to set

$$f_\lambda(t) = f_T(t) = f(t). \quad (13)$$

The input signal $\lambda_i(t)$ and $T_i(t)$ do not fulfil exactly the condition (11), but this condition is not quite irrelevant. From a very simplified point of view it is apparent that in the case of exothermic reaction, an increase in the concentration of the conductive reaction product is accompanied by an increase in temperature. Therefore, we arranged the dynamic characteristic of the measuring channels so as to fulfil the condition (12). But even if the condition (13) is fulfilled it does not mean that it is generally valid $F_i(t) = F_0(t)$ as can be seen from the Eq. (10), because $F_i(t)$ is in fact a nonconstant function of time. The magnitude of the dynamic error is very important with respect to the calculation of conductivity correction on temperature so as to obtain the values of concentration for every sampled moment. The transfer characteristic was found to be approximately expressed by

$$f(t) = 33.3 \exp(t/K); \quad K = 0.03 \text{ s.} \quad (14)$$

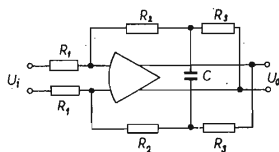


FIG. 3

Amplifying in the Temperature Channel

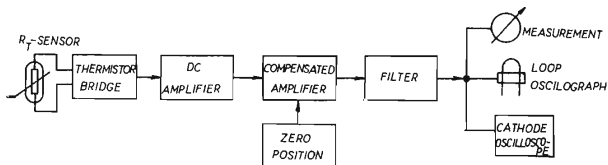


FIG. 4

The Block Diagram of the Temperature Channel

From Eq. (14) the amplitude and the phase frequency characteristic $A(\omega)$ and $\phi(\omega)$ can be derived. It holds that

$$A(\omega) = 1/(1 + K^2\omega^2)^{1/2}, \quad \phi(\omega) = \text{arctang}(-K\omega). \quad (15), (16)$$

For example, an amplitude distortion of 5% is reached at a frequency of 17.5 c.p.s. Properties of input signal fluctuations can hardly be deduced in advance. But their influence on dynamic error can be estimated according to results of some testing procedures.

Measuring Channels

For the abovementioned temperature-conductivity combination probe it was necessary to set up suitable electronic circuitry. The two circuits involved are mutually independent and hence they can be described separately.

Temperature channel. The circuit for temperature measurement (Fig. 2) consists of a Wheatstone resistance bridge with a stabilized dc voltage supply. The thermistor represents one of the arms of the bridge, the other arm being constituted by constant resistors and a potentiometer for zero adjustment. As the dynamic properties of the temperature channel are inferior to those of the conductivity channel, owing to the thermistor itself (the time constant of a single thermistor is $K = 0.4$ s) it was necessary to improve the transfer characteristic of the former channel by the means of a frequency dependent feedback in the dc compensated amplifier. Standard transistor differential operational amplifiers with feedback were used for amplifying both the temperature and the conductivity signals. The circuits of the compensated amplifier, operating as a PD stage, are shown in Fig. 3. The transfer function of the amplifier is expressed in Laplace transformation as

$$U_0/U_i = (R_2 + R_3)/R_1 + s(2CR_2R_3)/R_1. \quad (17)$$

The values of elements in the feedback loops can be determined from the given time constant $2CR_2R_3/R_1$ (which in the case of correct compensation ought to be equal to the time constant of the thermistor) and from the dc gain $(R_2 + R_3)/R_1$. The parameters of the compensated amplifier were set experimentally by changing the capacity C according to the unit pulse response of the total channel. The transfer characteristic with eliminated overshoots and a minimum time constant was considered optimum. In this way it was succeeded in obtaining a total time constant of the temperature channel equal to $K = 0.03$ s. This exceeds by more than one order of magnitude the value for the thermistor itself. A block diagram of the temperature channel is shown in Fig. 4.

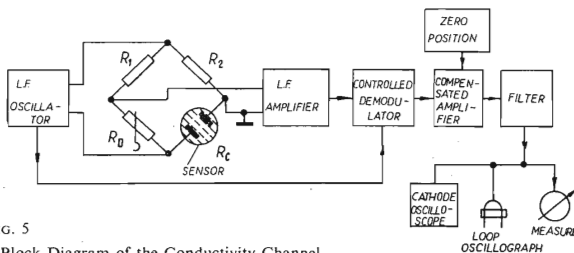


FIG. 5

The Block Diagram of the Conductivity Channel

As the maximum output voltage from the bridge was about 20 mV with respect to the assumed maximum temperature deviation it was necessary to use a further *dc* amplifier. A low pass filter was connected to the output of the channel to suppress noise and ripple and to improve the signal-to-noise ratio.

Conductivity channel. Two different principles are usually used in the measurement of conductivity fluctuations, *i.e.* the load resistor method and the bridge method. The former methods is suitable in the case of great amplitudes of conductivity fluctuations but has a lower sensitivity. We used the latter method for its high sensitivity and stability and because of the fact that the conductivity changes in the measured system did not exceed 20% of the average value. A block diagram of the total conductivity channel is shown in Fig. 5. The electrodes of the conductivity part of the probe are connected to one arm of the Wheatstone bridge, the other arms being formed by the resistance decade and by precision resistors. The large electrode was earthed. The bridge was supplied from an *ac* voltage source of 0.5 V and frequency 1 kc.p.s., which was sufficient for conductivity fluctuations up to 200 c.p.s. The main problem in designing the bridge resistors is to obtain a maximum sensitivity at a sufficient linearity for a maximum range of concentration changes. The nonlinearity of the total channel was not greater than 2% for a 20% change in conductivity. The output voltage from the conductivity bridge was amplified in the three-stage, low-frequency amplifier, and demodulated in the phase-sensitive controlled demodulator. This demodulator is of advantage in that it suppresses the disturbing voltage of frequencies other than the carrier frequency of the bridge oscillator. The other parts of the conductivity channel are similar to those of the temperature channel. To provide for the dynamic balance of both the channels it was necessary to use a compensating circuit with time lag for the conductivity channel. The compensation was carried out by an operational amplifier connected as a PI stage with a transfer characteristic (Fig. 5)

$$U_0/U_i = 1/(R_1/R_2 + CR_1s). \quad (18)$$

The adjustment of the proportional component R_1/R_2 and the time constant CR_1 was done similarly as in the case of the temperature channel. The fairly wide range of output voltage from both channels (10 V/5 mA) permits the use of various recording or evaluating devices. In our case we used both a three-loop oscillograph and a cathode oscilloscope with a photographic camera as a conductivity versus temperature plotter.

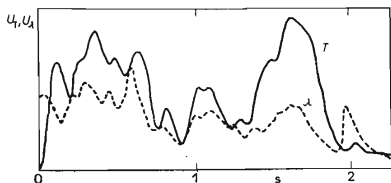


FIG. 6

A Typical Course of Local Temperature and Conductivity Recorded with an Oscillograph

U_T and U_λ are output voltages proportional to temperature and conductivity, respectively. The measurement is taken in the reaction zone.

Testing of Measuring Device Properties and Illustration of Results

Several tests were carried out with the measuring device in order to establish its correct function. The transfer characteristic of both channels were measured either by inserting the probe into warm acetic acid or by making the electric current pulse on electrodes located around the probe in a glass tube with flowing electrolyte.

Mutual independence of both channels was tested in such a way that measurements were taken in a liquid of constant temperature and concentration, either simultaneously for both quantities or for a single quantity only with the other channel switched off. In all cases the same indicated values were obtained. The effect of Joule heat is practically important if there is a dependency of indicated values of conductivity and temperature on the velocity of agitation. Another method for testing of mutual independence of both channels and correctness of their dynamic balance can be implemented in the following experiments.

If the reactor vessel is fed with two streams of acetic acid of different concentration but equal temperature, and measurements are made in the reaction zone, the output from the temperature channel should be constant. In the other case when the feed of the reactor consists of two streams of acetic acid with different temperatures but equal concentration, a plot of conductivity dependence on temperature should be drawn in the conductivity-temperature plane by the recording device (with no "hysteresis"). Such a result was indeed obtained. These results can also be interpreted as a certain proof of the equality of the effective volumes sampled by the conductivity and the temperature probes. However, the problem of the dynamic errors of the measuring system still remains.

A detailed analysis can be done only in connection with the purpose of the measurement. Usually, the object of measurement in a random process is not some instant but time averaged property and, therefore, it can be expected that the effect of dynamic errors on the results of measurement is also reduced during a procedure of evaluation of the output data. The calculation of temperature corrections for conductivity from instant values of temperature and conductivity for obtaining the value of instant concentration seems also to be affected by the dynamic error. The results of the abovementioned test with streams of constant concentration but different temperature do not quite determine the influence of these errors or the possibility of their

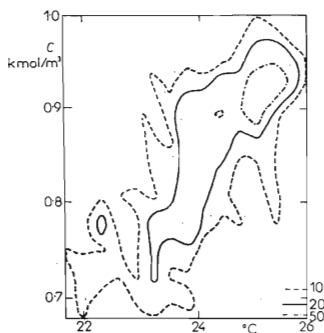


FIG. 7

Final Evaluated Concentration versus Temperature Frequency Function at the Same Conditions as in the Fig. 6

Curves represent the given frequency of occurrence of C , T coordinates. In this case 2000 (T , λ) values were read off with the step 0.0143 s.

