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High Frequency Inductance Manometer for Gaseous Reaction Studies[*1]

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A corrosion-free manometer which employs a variable inductor as a transducer has been devised. Its main part consists of a pair of small coils and a glass Bourdon bulb on which a thin aluminum disc is so attached as to be located between the coils. A manometer constructed as an example has the following characteristics: measurable (linear) range of pressure difference, 0—20 mmHg; minimum detectable pressure difference, 7×10^{-2} mmHg; temperature coefficient of zero-point drift, 0.2% of the full scale (20 mmHg) per degree; negligible temperature coefficient of output voltage per unit of pressure difference; limit of response time, 0.6 sec (under atmospheric pressure)—4 sec (1.1×10^{-3} mmHg). It is possible to extend the measurable range by changing the rigidity of the Bourdon bulb. From these results, it may be concluded that the manometer is useful in following and recording changes which have half-decay times of longer than a few seconds. When the manometer was applied to the study of the catalytic decomposition of formaldehyde on nickel wire, its usefulness was proved.

In order to follow the continuous change in the pressure of a reacting system, especially for the threshold of rapid change, it is necessary to use a transducer which converts the change into some electric quantity such as capacitance or inductance.

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There have been several devices in which a metallic diaphragm acts as a pressure-sensitive unit and also as a part of a capacitor.1)

It seems, however, better for chemical purposes that no metallic part be exposed to the reactant, which may be corrosive for or catalyzed by the metal surface.

One of the present authors2) had recently developed a high-frequency capacitance manometer to satisfy these requirements; this manometer consists of a glass Bourdon bulb with a small electrode attached as a capacitor. Though this device has proved to be sensitive enough, this advantage is negated to some extent by the rather unstable nature of the circuit, which is sensitive to such external disturbances as electrostatic induction.

On the other hand, if pressure-sensitive inductance is used instead of the capacitance, one can expect to improve the situation. As is well known, when a coil is placed near an electric conductor, its inductance for the alternating current will decrease as a result of the distortion of magnetic flux and the generation of an eddy current in the conductor.

The displacement of the conductor caused by the pressure change can, therefore, produce an unbalanced voltage in a high-frequency bridge which involves the coil as an arm.

This principle was adopted for the construction of an inductance manometer which is very stable and yet still sensitive. The present paper will describe the details of this device, and also some results of a kinetic study of the catalytic decomposition of formaldehyde on nickel wire, a study which was carried out as an example of its application.

Experimental

Construction and Circuit. The structure of the manometer is shown in Fig. 1. An aluminum disc, A (0.1 mm thick and 10 mm in diameter) was attached to the end of a glass Bourdon bulb, B, and a pair of small coils, L_1 and L_2, of 50 turns each with a ferrite core, C (3 mm thick and 4.2 mm in diameter) was fixed on a rod, D, opposed to one another, so that the disc was between the pair of coils.

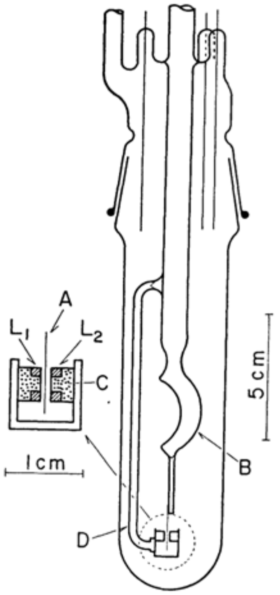

Fig. 1. Construction of manometer.

A Aluminum disc; B Glass Bourdon bulb; C Ferrite cores; L_1 and L_2, Detecting coils

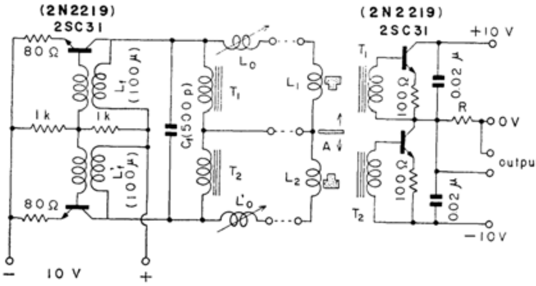

Fig. 2. Manometer circuit diagram.

The circuit, all transistorized, is shown in Fig. 2. An oscillating current of about one megacycle is generated in the circuit of the push-pull type, which mainly consists of a resonating capacitor, C_f, 2SC31 transistors, and coils, L_1, L_2, L_f and L_f', induces voltage drops in the primaries of the coupling transformers, T_1 and T_2, the values of which are made exactly the same by means of variable inductors, L_0 and L_0'.

The elements, T_1, T_2, L_0 and L_0', are shown in Figs. 3 and 4. Every coil, primary and secondary, in T_1 and T_2 has 50 turns. L_0 and L_0' are adjusted in a compensated way between 5-15 μH respectively, their sum (L_0+L_0') being kept at 20 μH. By this method, an almost constant sensitivity was obtained even if the initial position of the aluminum disc was slightly changed.

In this way, the rectified currents which come from the balanced detectors are superposed on a resistor, R, and the resultant differential current can be minimized to zero at the equilibrium position of the disc. The pressure change is then converted, through the changes in

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1) a) K. Sommermeyer, *Z. physk. Chem.*, **A155**, 208 (1931). b) C. H. W. Brookes-Smith and J. A. Colls, *J. Sci. Instr.*, **16**, 361 (1939). c) J. C. Lilly, *Rev. Sci. Instr.*, **13**, 34 (1942). d) J. C. Lilly, V. Legallais and R. Cherry, *J. Appl. Phys.*, **18**, 613 (1947). e) H. Matheson and M. Eden, *Rev. Sci. Instr.*, **19**, 502 (1948). f) H. Dibeler and F. Cordero, *J. Research NBS*, **46**, 1 (1951). g) M. L. Greenough and W. E. Williams, *ibid.*, **46**, 5 (1951). h) D. B. Cook and C. J. Danby, *J. Sci. Instr.*, **30**, 238 (1953). i) E. Rideal and A. J. B. Robertson, *ibid.*, **32**, 349 (1955). j) H. W. Drawin, *Advances in Vac. Sci. Tech.*, 274 (1960). k) K. G. Müller, *Vakuum Tech.*, **9**, 196 (1960). l) J. J. Opstelten and N. Warmoltz, *Advances in Vac. Sci. Tech.*, 295 (1960).

2) I. Yasumori, K. Nakada and S. Shida, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **82**, 285 (1961).

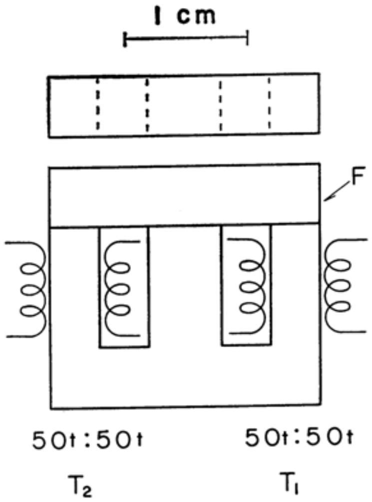

Fig. 3. Schematic diagram of coupling transformers, T_1 and T_2.

F E-I type ferrite core

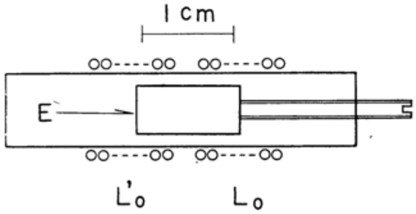

Fig. 4. Schematic diagram of variable inductors, L_0 and L_0'.

E Ferrite core

the displacement of the disc and the voltage drops in T_1 and T_2, into the voltage appearing on the resistor, R, a voltage which is easily recorded by a suitable device. The merit of the symmetrical circuit used is to extend markedly the linear range between changes in pressure and induced voltage, since many factors affecting the linearity cancel each other out. A well-regulated 10 V supply with a 15 mA current capability is needed.

On the basis of these improvements, a circuit with an excellent stability was obtained; this circuit showed a negligible zero-point drift.

Formaldehyde Decomposition on Nickel Catalyst. A kinetic study of the catalytic decomposition reaction of formaldehyde on nickel wire was made by the use of the present manometer system. The apparatus used consists of a gas-introducing system and a quartz reaction vessel (100 m*l*) with which the manometer is connected. The catalyst, a piece of nickel wire 6 m long and 0.15 mm in diameter, was oxidized in air of 100 mmHg at 500°C for 1 hr and then reduced in hydrogen of 70 mmHg at 350°C for 3 hr. This procedure was repeated several times prior to each run, so as to get reproducible results. The spectroscopic analysis of the nickel wire indicated that its purity was 99.99% by weight. The formaldehyde used was prepared by heating paraformaldehyde of a guaranteed reagent grade, obtained from the Yoneyama Chemical Co., at 70—80°C; the paraformaldehyde was degassed prior to the decomposition.

After the reaction system had been kept at a constant temperature, a suitable amount of formaldehyde was introduced and the pressure change was followed by the manometer.

Results and Discussion

An Example of the Manometer. In illustration of the present device, a manometer was constructed in which a glass Bourdon bulb sensitive to the displacement of the aluminum disc, 1×10^{-2} mm/mmHg, was involved. As may be seen from the curve in Fig. 5, the displacements against the pressure difference between inside and outside of bulb were quite linear, and no hysteresis was observed at any difference up to 30 mmHg.

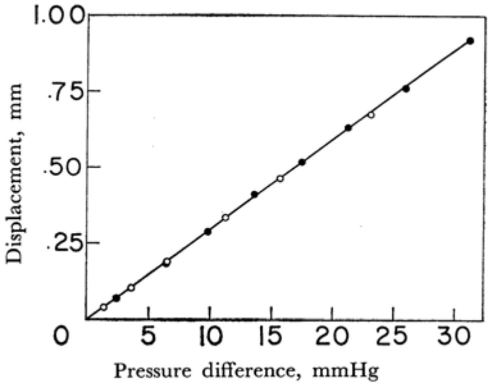

Fig. 5. Relation between pressure difference and displacement of the aluminum disc.

● First measurement
○ Repeated measurement

The manometer was then calibrated by the use of a recorder (Hitachi QPD-33) with a full-scale sensitivity of 1 mV and a mercury manometer equipped with a microscope. The characteristics of the manometer system thus obtained are shown in Fig. 6, where the output voltage, *V*, is plotted against the pressure difference, *P*, and the disc displacement, *X*. When $X<0.6$ mm or $P<20$ mmHg, an identical *P-V* relationship existed in the range of temperature between 21—57°C, while the maximum deviation of the output voltage from a straight line did not exceed 1.5% of the full-scale value, 20 mV. The temperature coefficient of the zero-point drift was less than 0.2% of the full-scale value (20 mV) per degree.

Further, the natural frequency of the bulb vibration and the half-decay time for its damping were determined, in order to inspect the fidelity in the face of rapid change, by means of a cathode-ray oscilloscope (Matsushita CT-310A) equipped with a camera (Canon CO-75-III). The frequency

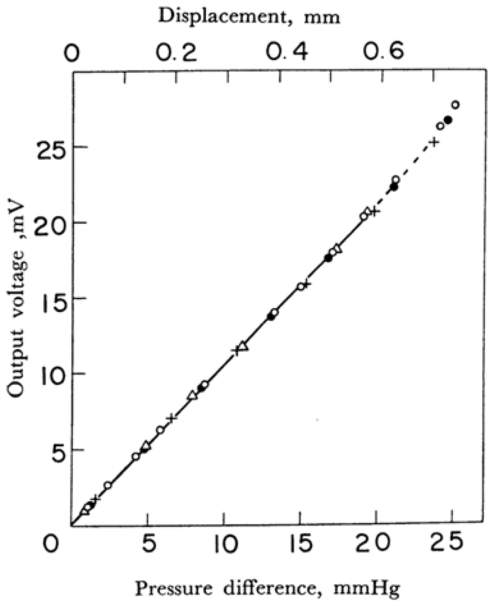

Fig. 6. Calibration line of manometer.

Measured at 21°C(●), 26°C(○), 41°C(△) and 57°C(+); R=11.6 ohms

was thus found to be 50 c/s and the half-decay time was estimated to be 0.06, 0.09 and 0.4 sec under pressures of 756, 1.1 and 1.1×10^{-3} mmHg of air respectively.

A brief discussion will be given here of the factors affecting the manometer sensitivity. When the current and resistance in the output circuit are denoted by I and R respectively, the sensitivity, S, may be defined by

$$S=\mathrm{d}V/\mathrm{d}P=R(\mathrm{d}I/\mathrm{d}X)(\mathrm{d}X/\mathrm{d}P)=Rk_1k_2$$

where k_1 is the efficiency of the system as a transducer, determined mainly by the nature of the electronic circuit, and k_2 is the rigidity of the Bourdon bulb. The use of a less rigid bulb or of a larger value of resistance may, therefore, increase the sensitivity.

However, any improvement along this line will be limited by the magnitude of the noise level. The noise observed in the present system can be classified into two categories, periodic noise and drift. The former is mainly generated by the continuous mechanical vibration of the Bourdon bulb and electrically by elements in the circuit, while the latter is caused by the change in the temperature of both mechanical and electrical elements.

The periodic noise had a relatively constant amplitude and gave lines a little wider on recorder charts. On the other hand, the drift showed only very slow, irregular changes in the output voltage. When the temperature of the manometer system was kept at ±1°C, the level of the periodic noise was much lower than that of the drift: the former was $\pm1\times10^{-3}$ mV and the latter, $\pm3.7\times10^{-2}$ mV. As may be seen in Fig. 6, the output voltage per unit of pressure difference is 1.08 mV/mmHg. It may, therefore, be concluded that the minimum detectable pressure difference was 7×10^{-2} mmHg.

The half-decay time for damping vibration should give the upper limit of the rate of the response of the manometer; therefore, the value multiplied by a factor of 10 will be the time limit required for the pressure change to be followed within an accuracy of 0.1%.

On the basis of the results described above, it may be concluded that the present inductance manometer, protected from the chemical action of reactive gas with its metallic part, shows excellent

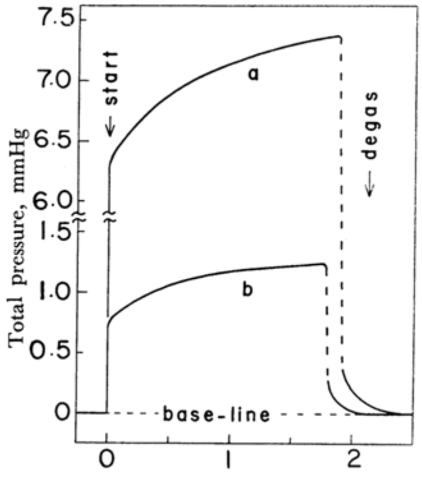

Fig. 7. Time course of the catalytic decomposition of formaldehyde on nickel wire.

a 161°C; b 180°C

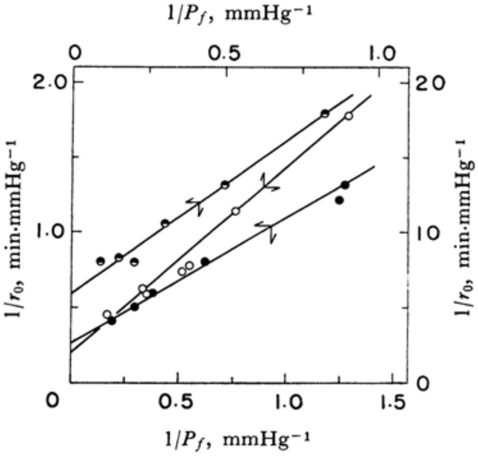

Fig. 8. Linear relationship between $(1/r_0)$ and $(1/P_f)$ in the catalytic decomposition of formaldehyde on nickel wire.

○ 120°C; ◓ 161°C; ● 180°C

stabilities upon variations in temperature, and that a device of this type will be most suitable for the measurement of pressure changes of 1.0—100 mmHg which have a half-decay time of more than a few seconds.

Catalytic Decomposition of Formaldehyde. Figure 7 shows the total pressure changes in the catalytic decomposition of formaldehyde on nickel wire. The initial rate of each run was derived from the slope of the curve in Fig. 7. The products were found by mass spectroscopy to be hydrogen and carbon monoxide.

The relationship between the reciprocals of the initial rate and of the partial pressure of formaldehyde, $(1/r_0)$ and $(1/P_f)$ respectively, is shown in Fig. 8. From these results, a rate equation was derived in the 250—310°C temperature range as follows:

$$r_0 = \frac{9\times 10^{22}}{g}\left\{\frac{0.35P_f}{(1+0.35P_f)}\right\} \exp(-15.6\times 10^3/\boldsymbol{R}T), \quad \text{molecules}\cdot\text{cm}^{-2}\text{sec}^{-1},$$

where g is the roughness factor of the nickel surface and where P_f is expressed in mmHg.

This equation suggests that the reaction proceeds through the decomposition of the formaldehyde adsorbed on the nickel surface, where the heat of adsorption is nearly equal to zero. The details of this study will be reported later in this Bulletin.

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