

Automated Manometric Apparatus¹

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Abstract

A manometric system has been developed for automatically performing hydrogenations, autoxidations and similar gas-liquid phase reactions. Incorporation of an ion chamber permits radioactive isotope experiments. Nonradioactive isotopes (such as deuterium and O¹⁸) are monitored by attaching the apparatus to a mass spectrometer. Automatic recording of gas volume and radioactivity establishes a permanent record and allows unattended operation. Use of a servomotor-driven syringe eliminates all mercury, including mercury leveling bulbs. The flow-through construction of the syringe permits circulation of the gas phase and, as required in isotopic experiments, obviates the dead space inherent in classical manometers. Basic electronics and readily available components enhance operation and construction. Typical hydrogenations with accompanying graphs showing gas uptake, reaction time and radioactivity concn illustrate the utility of the apparatus and the ease of collecting data.

Introduction

THE CLASSICAL MANOMETRIC SYSTEM (11) has an inherent dead space that precludes experiments involving mixtures of gases, such as with hydrogen isotopes in which complete mixing must be assumed. These units, whether they be automatic (9,13) or manual (8,11), usually contain mercury or electrical wires intermittently in contact with mercury. Obviously, such equipment requires constant attention and manipulation to level and clean the mercury, to polish corroded contacts and to prevent accidental spilling of the mercury.

An automatic manometric system has now been developed that eliminates the dead space and mercury, reduces the number of manual operations and is simple to operate. The outstanding components of the apparatus are a servo-driven flow-through syringe, an electromagnetic pump and a pressure sensor.

Description of Apparatus

Figure 1 is a block diagram of the complete manometric system showing the interconnection of parts. Solid lines indicate glass or plastic tubing between components of the closed reaction loop. Dashed lines indicate electrical connections. The direct drive from the servo to the syringe is shown as a dotted line.

This equipment is similar to the prototype unit used in a previous study on isotopic effects (2). Gas inlet system, monitor valve and dual pen recorder have not been altered. The reactor has been changed from a 25-ml to a 10-ml flask, the glass syringe to a metal flow-through one, and the sensor from a floating core manostat to a capacitance variety; the ion chamber is mounted directly on its pre-amp module instead of being remotely connected. In this manner, a small system volume was maintained, the syringe made unbreakable, greater differential pressure sensitivity (approx 0.01 mm of Hg) achieved and the amount of noise from the ion chamber decreased.

The electromagnetic pump used to circulate the gases within the closed reaction loop is presented diagrammatically in Figure 2. It is similar to some used by earlier investigators (4,10,12,14). The four ground-glass bead valves permit continuous gas flow with each stroke of the piston. Silent action is accomplished by eliminating the lower bumper and substituting a magnet which repels the downward stroke of the piston. One-coil operation, instead of the usual two of most previous designs, minimizes electronic circuitry. Pumping rate can be varied by electronic control from 1.5–200 cc/minute. The pump develops a maximum pressure of 2 in. of water, but this may vary according to tolerances of construction. Cleaning is facilitated by the removable ground-glass stoppers. Rubber bands can be used between the holding lugs on the stoppers to prevent them from loosening under pressure.

Figure 3 diagrams the automatic manometric syringe and illustrates its flow-through construction and servo drive. Points A and B denote outlet and inlet, respectively. An "O" ring (not shown) located at the tip of the plunger makes a vacuum-tight seal. Limit switches prevent overtravel, and a volume switch allows equipment shutdown at a predetermined gas uptake. The 10-turn potentiometer-transducer converts the displacement of the syringe into an electrical potential for recording gas volume changes.

A schematic of the electronic control circuits is shown in Figure 4. The left half of the schematic indicates power supplies and the commercially available servo amplifier (Brown "Elektronik," 359659-3) (15). A description of these typical power units can be found in most electronic texts (1,7). The 26.5-v supply is regulated by two zener diodes, 1N2988 B and HS-8. This regulation is necessary to stabilize the voltage for the sensor and recorder transducer.

An astable (free-running) multivibrator (V1), shown in the upper right quadrant of Figure 4, forms the pulses that actuate the pump drive. Varying the "rate" control potentiometers alters the speed of pumping. A cathode-follower power amplifier (V2) was chosen as the pump drive because of its current capacity and because it reduces the high-voltage hazard at the coil. The semiconductor diode (M150) is an essential part of the circuitry for proper operation. This diode decreases, to the point of elimination, collapsing voltage transients across the coil to maintain smooth and constant pumping action.

The lower right quadrant of Figure 4 denotes the recorder and servo controls. Any recording instrument from a 100-mv to a 1-mv type may be used by adjusting the "range" switch and "calibrate" po-

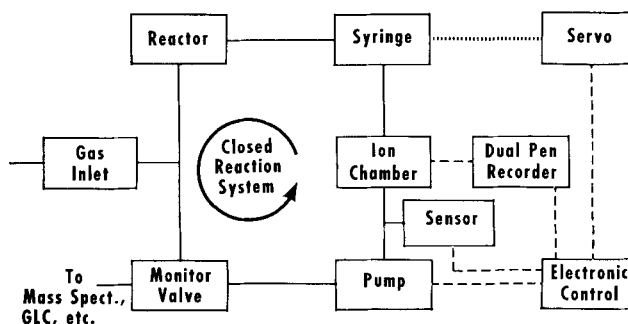


FIG. 1. Block diagram of automated manometric system.

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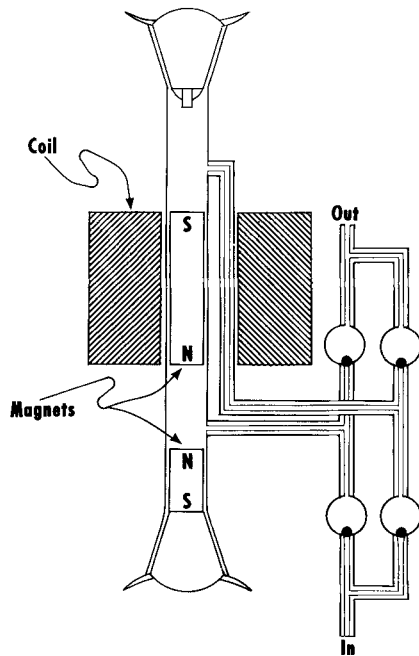


Fig. 2. Electromagnetic pump designed for system and equipped with glass bead valves.

tentiometer. The recorder 5K transducer forms part of a voltage divider and is mechanically connected to the servo as shown by the dotted line. Linearity of a recording is directly related to the tolerance of the transducer, which is $\pm 0.25\%$. The servo may be controlled either manually or automatically by positioning switch S1 (A-C).

A few intrinsic troubleshooting aids are included: A neon indicator on the multivibrator (V1) and shorting the off position of S1. Failure in the pump circuitry can be seen if the pump piston is not reciprocating (V2 operating) or the neon light is not flashing (V1 operating), or both. Similarly, noisy or erratic operation of the servo system can be traced to the

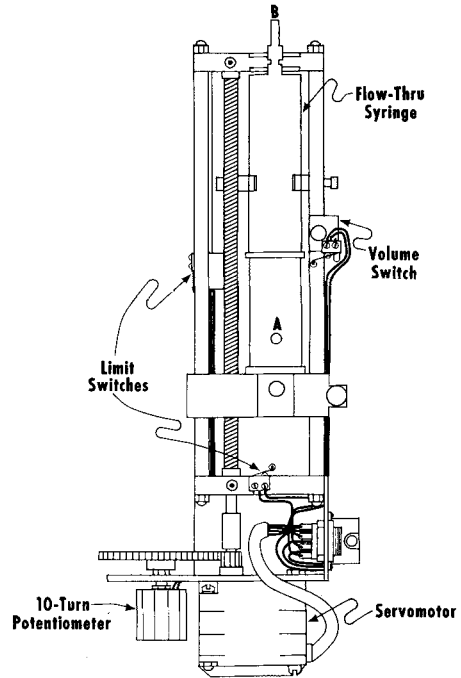


Fig. 3. Automatic manometer mechanism.

sensor or following circuitry by placing S1 in the off position; if the trouble persists, it is in the amplifier or servomotor; if the erratic operation ceases, it is in the sensor.

Calibration and response time are important in using the automated manometric apparatus shown in Figure 5. Calibration is accomplished by manually positioning the manometric syringe to either extreme, injecting or withdrawing 50 cc of air to move the syringe automatically by exactly this amt, and then adjusting the calibrate potentiometer for a reading of 50 cc. Similarly, response time can be determined by injecting 50 cc of air as rapidly as possible and by noting the time required for the apparatus to compensate.

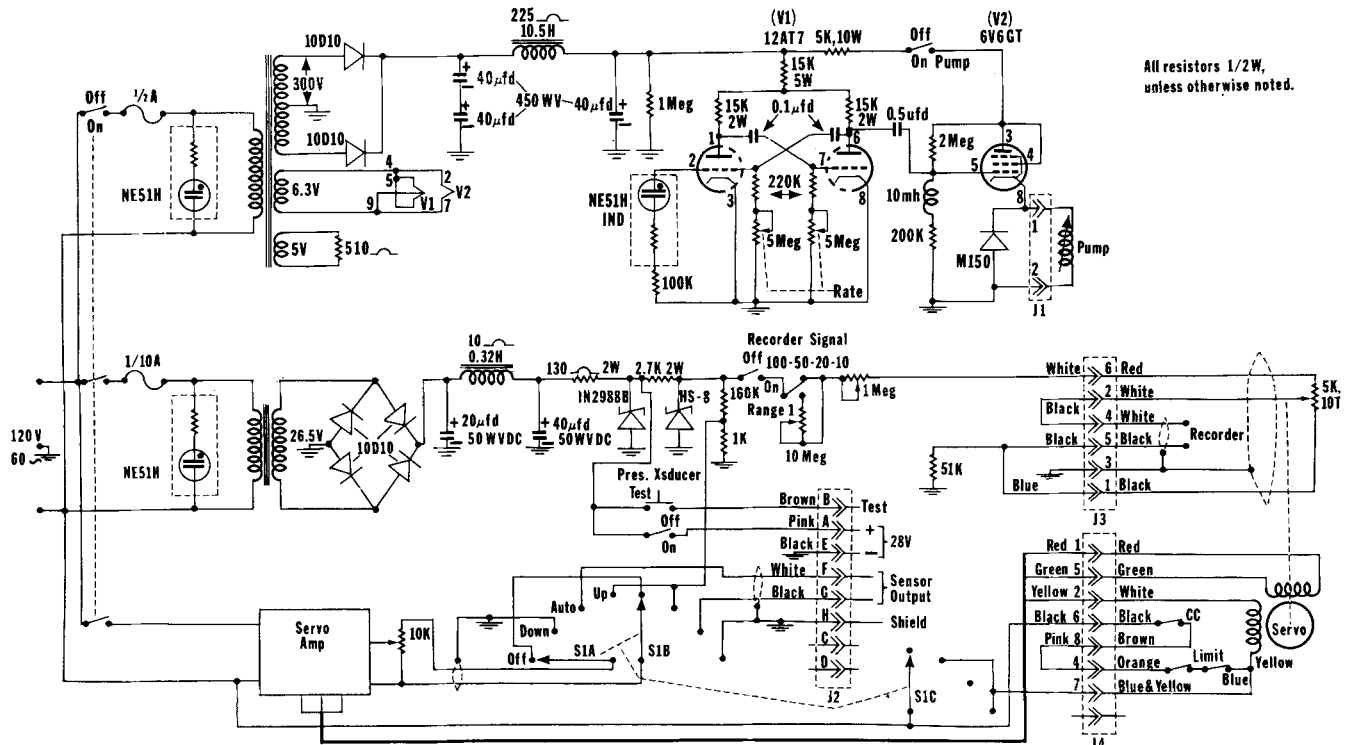


Fig. 4. Schematic of electronic control system.

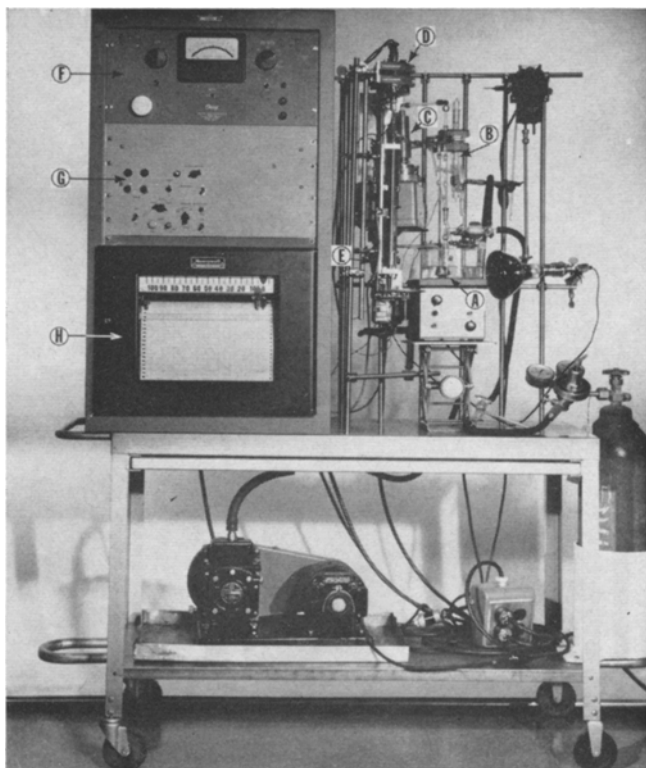


Fig. 5. Note the compact arrangement of the closed reaction system: (A) Reaction flask with associated oil bath and magnetic stirrer, (B) electromagnetic pump, (C) ion chamber, (D) differential pressure sensor, and (E) syringe mechanism. Accessories: (F) electrometer, (G) electronic control chassis, and (H) two-pen recorder. Cart mounting provides mobility.

The minimum time is 1.5 min, whereas the maximum time is limited only by recorder speed and chart length. Thus, the system can be used for all but the most rapid reactions.

Experimental

The functioning of the apparatus was confirmed by conducting two types of hydrogenations. The first verified previous research (2) using tritium and indicated no isotopic effect; the second simulated an isotopic discrimination. In both reductions, atmospheric pressure, a temp of 40C, a commercial catalyst consisting of 5% palladium-on-carbon powder and methyl oleate were used. Also, the catalyst-to-ester ratio was approximately 1:4 (wt to wt), and 0.30–0.40 g of ester was used for each reaction.

The procedure for the first hydrogenation experiment—flushing the system with hydrogen, introducing tritium, equilibrating the electronic equipment and initiating the reaction—was identical to that given earlier (2). A slight modification was necessary for the second hydrogenation in which a vial, containing a few milligrams (approx 0.3 mg) of C^{14} labeled $BaCO_3$, was inserted into the system. After the final filling of the apparatus with hydrogen, 1 cc of a 30% solution of perchloric acid was injected into the vial to release the radioactive CO_2 . The reaction was initiated by injection of methyl oleate into the reaction flask after equilibration of the radioactivity.

Results

Typical results for the first class of hydrogenations are shown in Figure 6 which is a graph automatically recorded as the experiment progresses. The ease with which data can be obtained is obvious. The starting point of the reaction (A) need not be labeled since

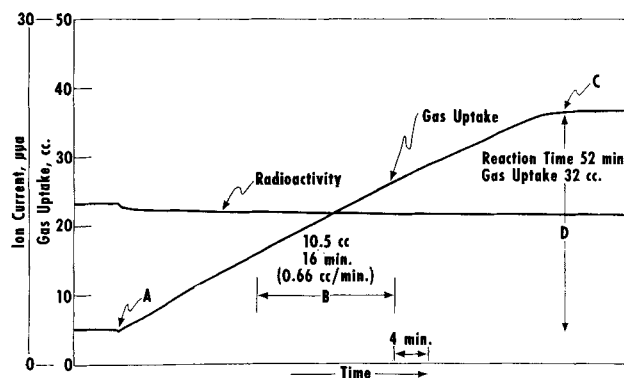


Fig. 6. Hydrogenation of methyl oleate with a mixture of hydrogen and tritium gas in the manometric system.

the equipment compensates and records a change in volume caused by injecting the 0.3 ml of ester. Saturation (C) is easily noted by the leveling off of the curve indicating cessation of gas uptake. The time difference between these two points is the reaction time. Rate of reaction can be determined by using any linear portion (B) of the curve. Previous calibration of the chart in cc/div. permits immediate calculation of gas uptake (D) during the reaction. For example, in the first hydrogenation reaction time was 52 min; reaction rate, 0.66 cc/min; and gas uptake, 32 cc.

Likewise, the radioactivity trace readily indicates the degree of isotopic discrimination by remaining unchanged or by an increasing or decreasing slope, the former showing no isotopic effect and the latter, a selective absorption of the nonradioactive atom or radioactive atom. Since there is no significant change in the radioactivity curve in Figure 6, no isotopic discrimination occurs under the conditions used.

Results from the second hydrogenation experiment on simulation of isotopic discrimination are shown in Figure 7. A typical gas-uptake curve demonstrates initiation of the reaction (A), a rate of reaction of 0.45 cc/min (B), saturation (C), a 64-min reaction time; and 33 cc of gas used (D). The radioactivity trace shows an increase in concn. This increase is directly proportional to the amt of gas uptake as shown by comparing the ratio of gas uptake to total gas volume (33:105 or 0.314) and by comparing the ratio of the change in radioactivity concn to total concn (using chart division 47:150 or 0.313, for simplicity). This means that the radioactive atom did not enter into the reaction but became more concd as the hydrogen was absorbed. The anomalous behavior of the radioactivity trace at the point of reaction initiation should be noted (Figs. 6 and 7). When the methyl oleate is injected, on some occasions the radioactivity suddenly increases and, on others, decreases. Whether it is quenching of ions, a release by displacement of catalyst-bound radioactivity, or some other effect is still a matter of speculation. Despite these initial inconsistencies and equilibrations, the linearity of the curve can be easily determined if a straight line is drawn from the initiation point over the length of the reaction trace in Figure 7.

Discussion

A persistent need has existed in physical-chemical, organic and biochemical research for following gas exchanges volumetrically. This demand has been met quite universally by the manometric technique with its variety of modifications. One handicap of manome-

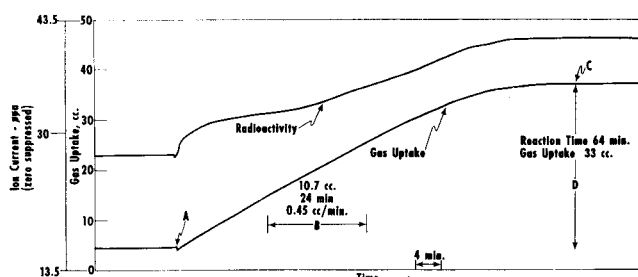


Fig. 7. Simulated isotopic effect in an automatic manometric apparatus.

try is the requirement of continuous attendance—equilibrating levels, reading and recording. Not only does our new system automatically perform these operations, but it also obviates still another disadvantage of manometry, that of “dead” or uncirculated gas space. This restriction limits the applicability of the manometer for experiments involving gas exchange, such as oxygen and carbon dioxide in photosynthesis or isotopic exchange experiments involving hydrogen, deuterium and tritium gas (2). The use of a flow-through syringe eliminates this unmixed gas volume and mercury vapor contamination. In addition, eliminating the need for reading glass burets makes possible applications well above or below atmospheric pressures.

The circulating gas system also makes this arrangement amenable to monitoring procedures for radioactivity as illustrated here, or for mass spectrometry as previously described (2). A variety of other monitoring procedures may be suggested, such as paramagnetic oxygen analysis or abridged IR spectro-

photometry for carbon dioxide and other gases. To take advantage of the numerous monitoring possibilities, the equipment was made mobile by cart-mounting. This arrangement permits moving the system to special MS, GLC, radioactive or other laboratories. Also readily apparent are application to routine and repeated gas absorption investigations as are involved in evaluating catalysts for activity and selectivity (8).

Many components in the system may be fabricated in a local glass or metal shop. At present, the pressure sensor (Trans-Sonics, No. E2821) (5) must be purchased and is the most costly part of the automation due to its high sensitivity and miniaturization. However, simpler types are available (6) and are now being evaluated (3).

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Dimer Acid Structures. The Thermal Dimer of Methyl 10-*trans*, 12-*trans*, Linoleate¹

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Abstract

Thermal dimerization of the conjugated 10-*trans*, 12-*trans* linoleate (250C, 5 hr) produced a dimer whose structure is shown to be that of the Diels-Alder reaction between two molecules of monomer, with one molecule acting as diene, and either one of the two double bonds of the second molecule acting as dieneophile. This produces four skeletal isomers of a tetrasubstituted (1,2,3,4) cyclohexene structure with α - β unsaturation on one chain. The isomers formed depend on whether the 10 or the 12 double bond acts as dieneophile, and whether the monomers add “head to head” or “head to tail.” Evidences for the structures include chemical analyses, ozonolysis, nuclear magnetic resonance, IR and UV spectrometry and particularly mass spectrometry of the distilled dimer, of the completely hydrogenated dimer, and of the aromatized dimer formed by catalytic dehydrogenation. The hydrogenated dimer can be separated into two components by TLC. These are probably related to “head to head” vs. “head to tail” addition.

Introduction

IT WAS PREVIOUSLY SHOWN (1) that the conjugated *trans* linoleate isomer, 10-*trans*, 12-*trans* linoleate was polymerized by heat at a much faster rate than normal 9-*cis*, 12-*cis*, linoleate, or alkali conjugated (9-*cis*, 11-*trans* plus 10-*trans*, 12-*cis*) linoleate. The reaction was second order, and the ratio of dimer to trimer was quite high, compared to other linoleate isomers.

It was suggested that the dimerization was a Diels-Alder addition, with one of the double bonds of one molecule acting as dieneophile, adding to the conjugated diene of the second molecule. The rapid rate of reaction of the *trans-trans* isomer was in accord with other data on 1,4 disubstituted 1,3 dienes. Four isomeric skeletal structures would be expected: (10 refers to the 10 double bond acting as dieneophile; A means that carboxy-containing groups are on adjacent carbons). Isomers due to *cis*, *trans* isomerism on the cyclohexene ring are also possible.

The present work is a further study of the structure of this dimer. It confirms the proposed cyclohexene structure expected from a Diels-Alder addition. The principal points in this structure proof are: 1) correct C & H analyses and mol wt; 2) mass spectrometry

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