Gas Analysis With Pulsed Vacuum Networks *

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Abstract

A molecular-flow network theory applicable to volumes interconnected by small orifices or porous membranes is discussed. Parameters which describe the properties of such orifices and membranes are defined. The basic theory is then extended to cover various cases of pulsed operation with mixtures of gases having different molecular weights. The mass-dependent impedance of an orifice or porous membrane makes it possible to use molecular-flow networks as gas analyzers. Experiments with molecular-flow networks at pressures up to 100 Torr are summarized. A simple automatic measurement of the pressure in a pulsed network can give the effective molecular weight of a gas sample with an accuracy of a few parts per thousand. More elaborate computer analyses of output pressure waveforms appear capable of giving at least semiquantitative information about the molecular weights and partial pressures of the various gases present. Instruments of this type may be useful for analysis of planetary atmospheres.

1. Introduction

Equations similar to those used to describe electrical networks can be used to describe the flow of gases if pure molecular-flow conditions exist. These equations include the molecular-flow

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equivalents of Ohm's and Kirchoff's laws. They have been used by Dushman (1962), Barnes (1964), and many others for analyzing problems involving the steady-state flow of pure gases in simple vacuum systems. Teubner (1962), has used a similar approach to analyze selected cases of non-equilibrium molecular flow of pure gases.

It is well known that the impedance offered to a particular gas by an orifice or porous membrane operating under molecular-flow conditions is dependent on the molecular weight of the gas. It follows that networks consisting of chambers interconnected by orifices or porous membranes would also be expected to show mass-dependent characteristics under such conditions. Because of the statistical nature of the molecular-flow process, it would further be expected that the responses of such "molecular-flow networks" might contain information about the actual gases present and their relative abundances. This paper describes the results of attempts to test these suppositions.

2. Theory of Molecular-Flow Networks

From kinetic theory and from the definitions of the parameters involved, the following relationships hold in a molecular-flow network in which an isotopically pure gas is flowing at constant temperature:

(a.) For an orifice, porous membrane or similar component which impedes flow

$$\Delta P = QR \qquad (1),$$

where ΔP is the pressure difference across the component in Torr, Q is the gas current in Torr-liters/sec., and R is the impedance in seconds/liter for the particular gas involved. The impedance R is the reciprocal of the conductance, or pumping speed, of the component.

The mass-dependence of the impedance at constant temperature can be expressed by the relationship

$$R = KM^{\frac{1}{2}} \qquad (2),$$

where M is numerically equal to the molecular weight of the gas in atomic mass units and K is a constant characterizing the particular component. K will be referred to as the unit-mass impedance.

(b.) For a chamber in which the pressure is changing,

$$\frac{dP}{dt} = \frac{Q}{V} \qquad (3),$$

where P is the internal pressure, Q is the rate of arrival of gas and V is the volume of the chamber. The pressures are assumed to be sufficiently high for adsorption effects to be negligible.

(c.) The algebraic sum of the pressure differences around the elements of a closed path in the network is zero, i.e.

$$\sum_{\text{closed path}} \Delta P = 0 \qquad (4),$$

It is assumed that molecular velocities are randomized so that the concept of a scalar pressure at a given point in the network is valid.

(d.) At a junction point the algebraic sum of the arriving (or departing) gas currents is zero, i.e.

$$\sum_{\text{junction point}} Q = 0 \qquad (5),$$

The junction point must be defined so that it is not inside a volume, although it may be considered infinitesimally close to the volume.

If a gas mixture is present in a molecular-flow network, the situation becomes more complicated. The relationships quoted above will hold separately and simultaneously for each isotopically pure gas species. If there are n gases, of which the j^{th} gas is typical, the following relationships result:

$$\text{For an impedance, } \Delta P = \sum_{j=1}^{n} \Delta P_j = K \sum_{j=1}^{n} Q_j M_j^{\frac{1}{2}} \qquad (6),$$

$$\text{For a chamber, } \frac{dP}{dt} = \frac{d}{dt}\left(\sum_{j=1}^{n} P_j\right) = \frac{\sum_{j=1}^{n} Q_j}{V} \qquad (7),$$

$$\text{For a closed path, } \Sigma \Delta P_j = 0 \text{ for all } j \qquad (8),$$

$$\text{For a junction, } \Sigma Q_j = 0 \text{ for all } j \qquad (9),$$

Thévenin's theorem, Norton's theorem, portions of ac electrical theory and the concepts of output and input impedance can also be shown to apply to molecular-flow networks.

3. A Single-Membrane Pulsed Network

The simplest possible molecular-flow network is the analog of an RC electrical circuit. This case has been analyzed for pure gases by Lawson (1966) and Teubner (1962). At the left of Fig. 1 is a simplified version of the actual layout, with a symbolic representation on the right. If a gas mixture is entering the initially empty volume V from a source at total pressure P_{in}, the internal pressure waveform can be obtained by applying equations (6) - (8) and solving the resulting differential equation. The solution is of the general form

$$P_{out} = \sum_{j=1}^{n} P_{j,in} \left[1 - \exp (-t/VKM_j^{\frac{1}{2}}) \right] \qquad (10),$$

The constants $P_{j,in}$ and M_j respectively represent partial pressures and molecular weights in the incoming gas.

The simple arrangement shown in Fig. 1 is somewhat inconvenient in practice because the chamber must be re-evacuated before each waveform is recorded. An alternative system employs the vacuum equivalent of a symmetrical vibrating capacitor. This makes it possible to record repeated waveforms with the same gas sample. Such a system is being used to study the properties of the porous silver membranes used in these experiments. Pore diameter is 0.2 microns. A piece having an area of 1 $cm.^2$ exhibits a unit-mass impedance of about 5 seconds/liter.

Figure 2 shows the linear relationship between the square root of the molecular weight and the time constant for one of these systems when operated with pure gases at a pressure of 1 Torr. The rather small variations in these time constants as the pressures were raised to 100 Torr are shown in Fig. 3. These results, with those of

Owens (1965) and Christian and Leck (1966), show that porous membranes suitable for use in molecular-flow networks are readily available in several different materials.

The pressure-time waveform given by equation (10) is not itself exponential unless there is only one gas present. However, it can be approximated by an exponential to obtain an effective molecular weight, as suggested by Eden (1951). For a binary gas mixture in which the identities of the two gases are known, this immediately fixes the percentage composition. Alternatively, if the quantities M_j were known, the partial pressures could in theory be determined by the solution of an equal number of simultaneous equations. These could be derived from equation (10), a knowledge of the values V and K from prior calibration, and a knowledge of a sufficient number of points on the pressure waveform. Finally, it is theoretically possible to solve for P_j and M_j simultaneously under suitable conditions. These possibilities were pointed out by Kendall (1966) and have been confirmed in principle by subsequent digital and analog calculations with simulated data.

4. A Three-Membrane Pulsed Network

A more advanced system, which is being studied for possible use in a Mars soft landing experiment, is shown in Fig. 4. The piston-type inlet valve injects 0.01 cm.^{3} of gas each time it is acuated. Volumes V_1 and V_2 are intentionally made slightly different, giving an output waveform of the type shown. This waveform is intended to be fed to a telemetering transmitter and ultimately to an Earth-based data processing system, as shown in the diagram. After a sequence of repeated analyses, the pressure transducer would be used to monitor the total surface pressure. Data analysis would be based on the techniques mentioned in the previous section.

The apparatus enclosed by the dotted line in Fig. 4 has been completed. It fits inside a cube with a 10 cm. edge and weighs approximately 1.5 kilogram with batteries, transducer and transducer circuitry. The time from gas injection to the first point where the pressure difference first passes through zero is a sensitive and convenient measure of the square root of the effective molecular weight. This time is reproducible with a standard deviation of about 1 part in 600 over a large number of successive analyses. By subtracting electrically-produced waveforms characteristic of pure gases from the pressure waveform, gross structure indicative of the presence of lighter or heavier constituents can easily be seen without any further data processing. Tests on this apparatus are continuing.

5. Discussion

Analyzers based on molecular-flow networks have certain unique advantages combined with their obvious disadvantages. They are simple and rugged. The spectra contain no fragment peaks. Samples can be reused indefinitely. There are no hot filaments to cause changes in sample gas composition. They can operate at comparatively high pressures, so that no elaborate pumps are required.

The recent availability of membranes with holes an order of magnitude smaller than those now in use may even make it possible to operate these analyzers at atmospheric pressure.

References

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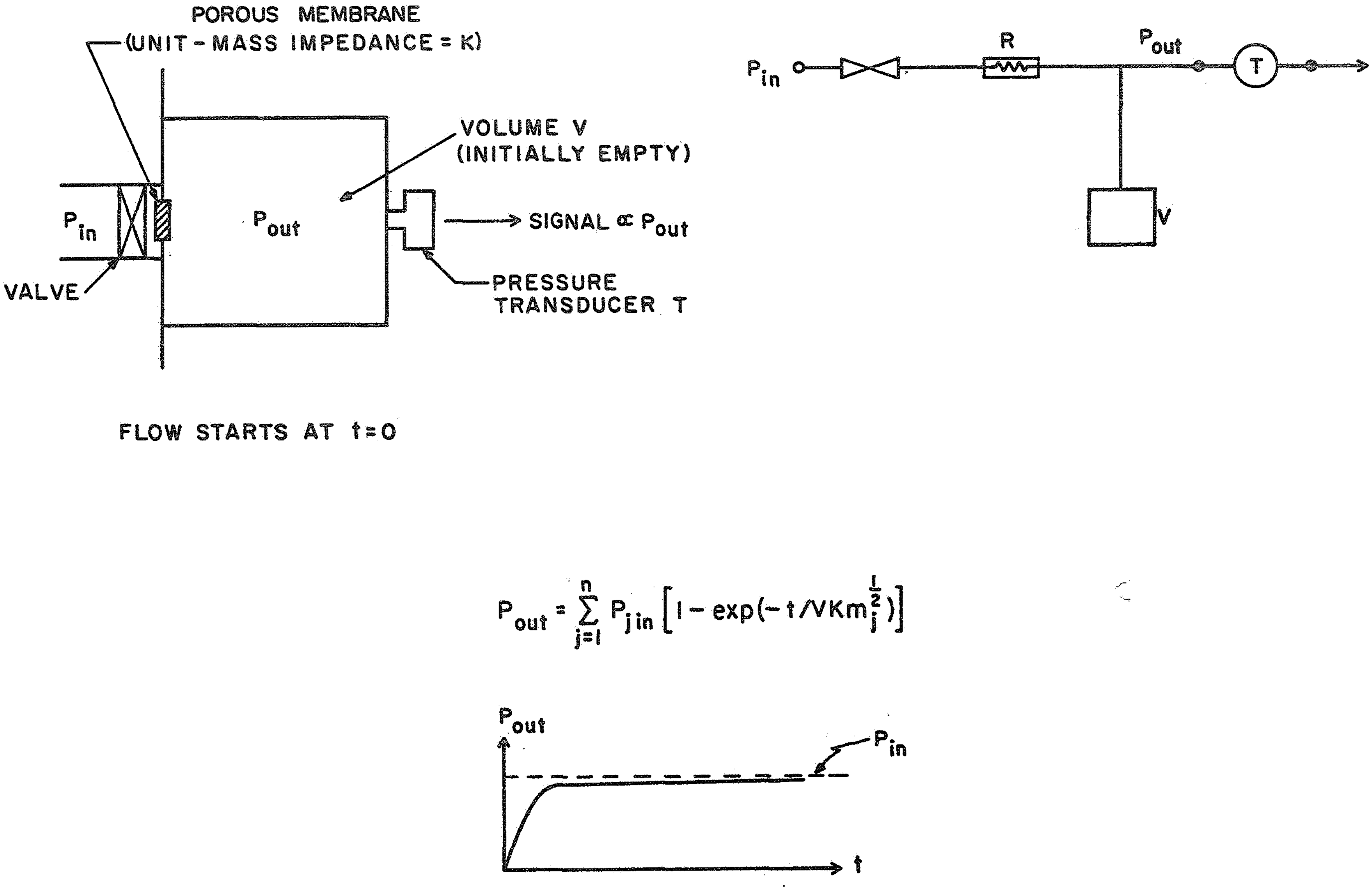
Figure Captions

1. Molecular flow into enclosed volume.
2. Molecular weight vs time constant of RV network at 28° C. and 1.0 Torr.
3. Pressure dependence of time constants for various gases in RV network at 28° C. Membrane hole size 0.2 μ.
4. Proposed network for planetary atmosphere analysis.



$$P_{out} = \sum_{j=1}^{n} P_{j\,in}\left[1 - \exp(-t/VKm_j^{\frac{1}{2}})\right]$$

FIGURE I. MOLECULAR FLOW INTO ENCLOSED VOLUME

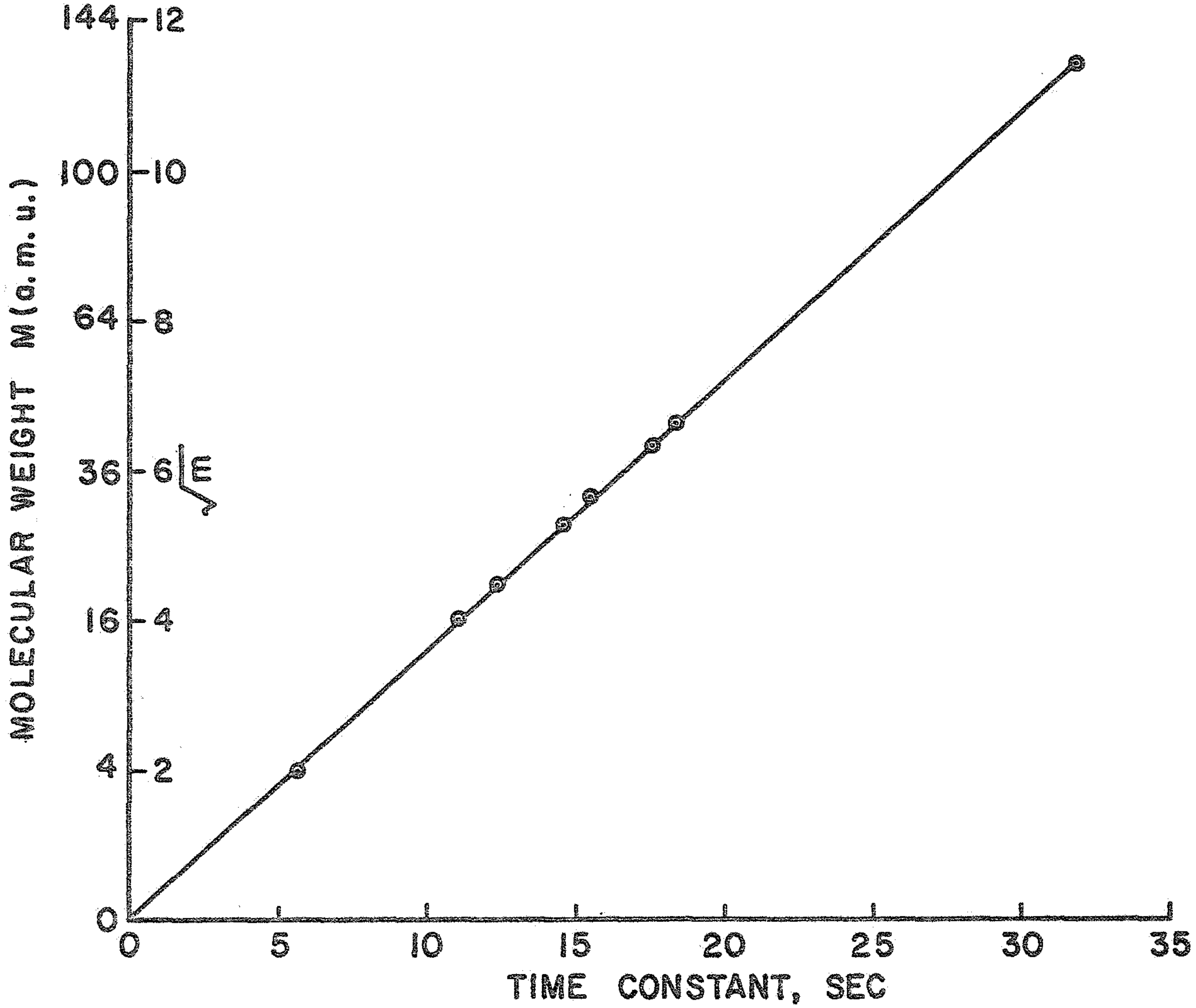


FIG. 2. SQUARE ROOT OF MOLECULAR WEIGHT VS TIME CONSTANT AT 28° C, 1.0 Torr

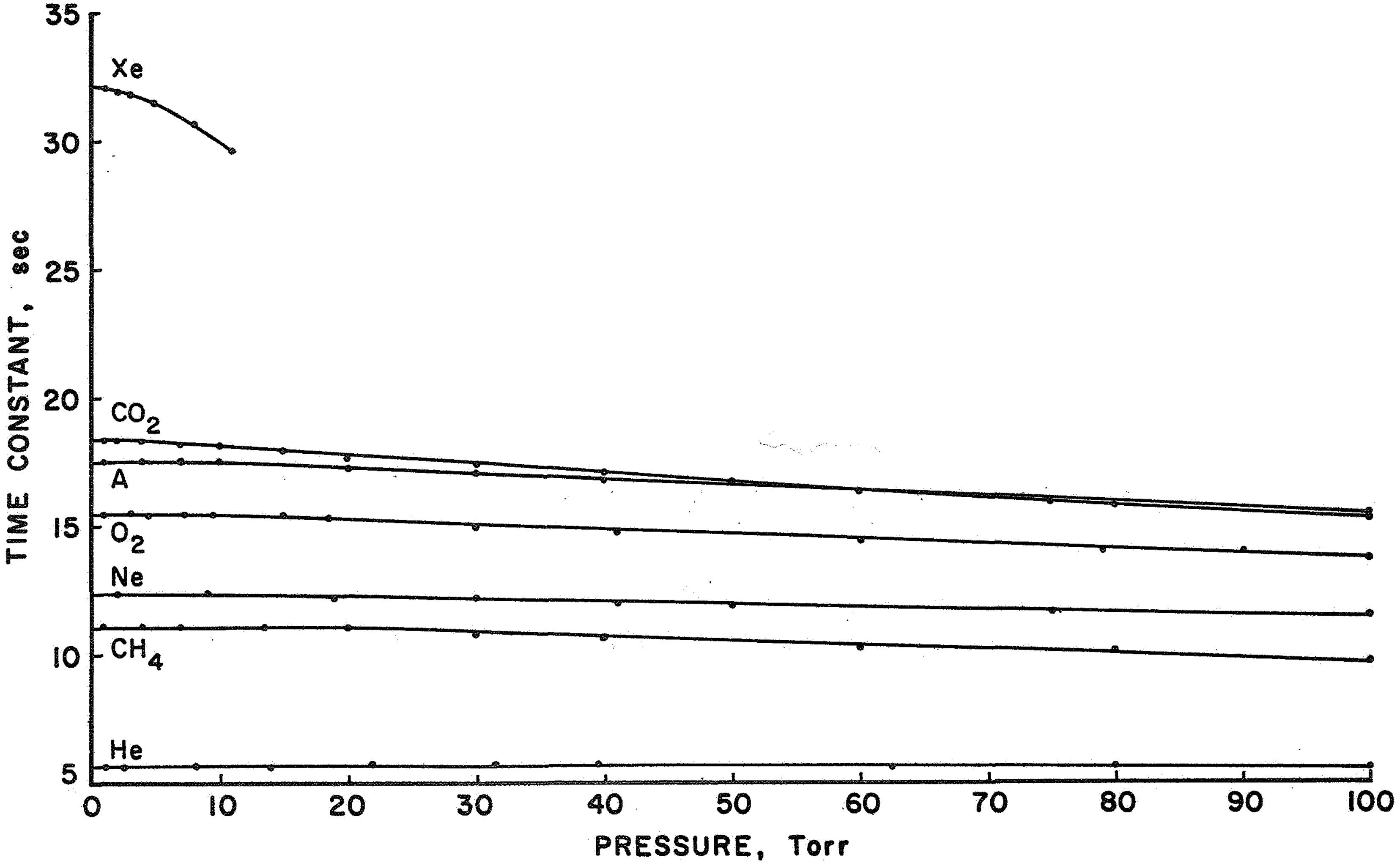


FIG. 3. TIME CONSTANTS FOR VARIOUS GASES FLOWING THROUGH .2μ-HOLE MEMBRANE AT 28° C

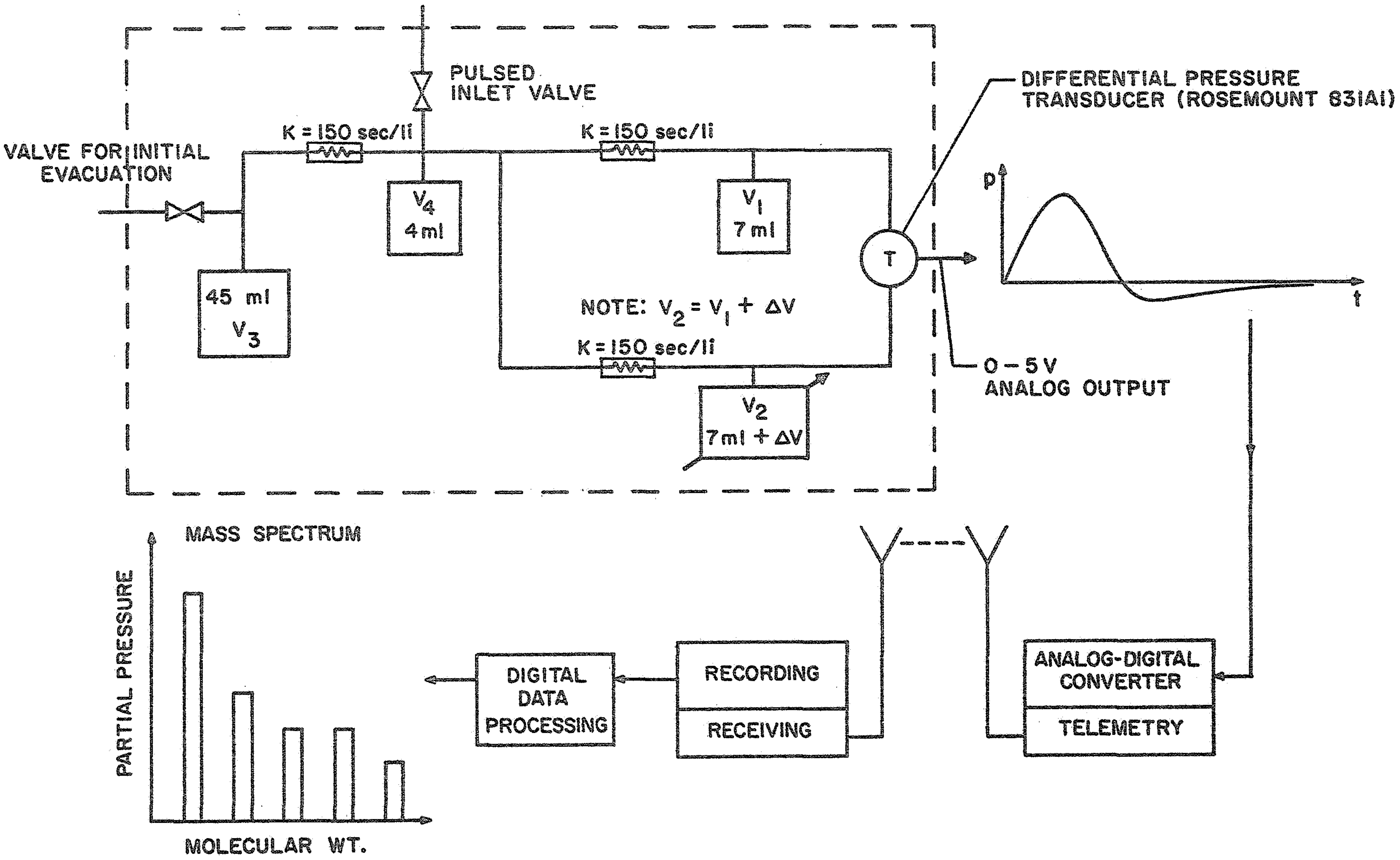


FIGURE 4. NETWORK PROPOSED FOR PLANETARY ATMOSPHERE ANALYSIS