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## THE NON-LINEAR BEHAVIOR OF A GAS DENSITY DETECTOR —A THEORETICAL BASIS

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### SUMMARY

A detailed theoretical analysis of the gas density balance detector has been conducted and a general relationship for the detector response (that involves the detector dimensions, molecular weight of the carrier gas and the solute, the reference to carrier gas flow ratio, the mole fraction of the solute in the column effluent as major parameters) has been developed. Consequences of the non-linear terms have been analyzed and the theoretical predictions have been compared with the available experimental data. A new set of criteria for the linear response conditions have also been advanced.

### INTRODUCTION

The gas density balance detector for chromatographic analyses was first introduced in 1956<sup>1</sup>. The present detectors<sup>2</sup> are, however, based on a simplified design<sup>3</sup>

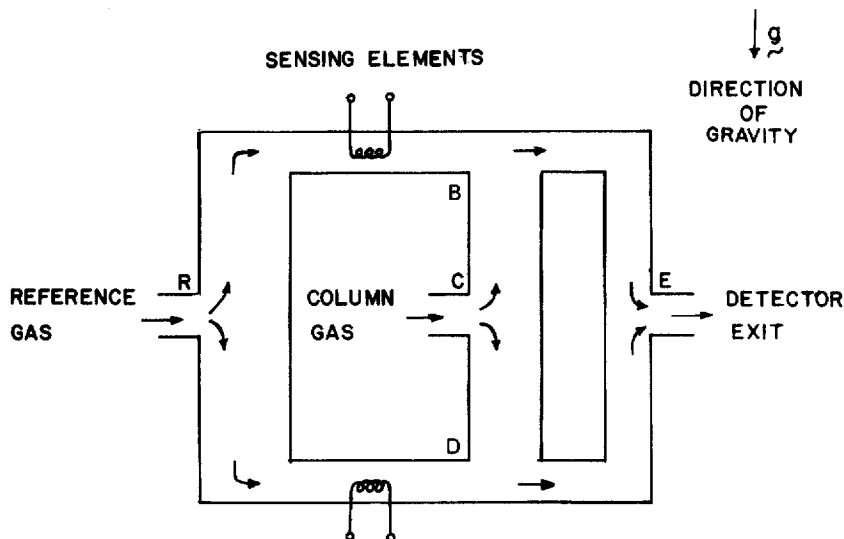


Fig. 1. Schematic diagram of the gas density balance detector.

which, as shown in Fig. 1, basically consists of three vertical conduits that are interconnected. A reference gas enters the vertical conduit at the left and is split into two parts that flow in parallel over the sensing elements. Carrier gas from the chromatographic column enters the vertical conduit in the middle. Carrier and reference gases combine and exit from the third vertical conduit at E. Reference gas is chosen to be the same as pure column carrier gas and, consequently, as long as there is no solute present in the carrier gas the flow of the reference gas over the sensing elements (which are part of the Wheatstone Bridge) is not disturbed. When, however, a solute with a density different than that of the carrier gas enters the cell at C, the density of the gas in the vertical conduit BD and consequently the pressure at D changes, altering the balanced flow of the reference gas over the upper and lower sensing elements. The change in the flow of the reference gas over the sensing filaments leads to a change in their temperature and in turn to a change in the resistance between the upper and lower elements. This unbalance is recorded as a chromatographic peak.

This detector has a number of interesting features. Its design is such that solutes do not come in contact with the sensing elements, and therefore it is non-destructive and also suitable for analysis of corrosive substances. The response, being a result of density variations, is independent of the details of the chemical structure of the solute that is under analysis. Since density is related to molecular weight, the detector is suitable for molecular-weight determinations and in fact is being used for such a purpose in mass chromatography<sup>4,5</sup>.

The behavior of this detector has been the subject of a number of publications<sup>3-12</sup>. The effect of parameters such as the nature of the carrier gas, reference and column flow rates, temperature of operation, and the detector bridge current on the sensitivity of the detector has been studied. Limits on detection and the range of linearity with sample size have also been studied. Furthermore, the detector has been compared with and used for the calibration of thermal conductivity and flame-ionization detectors<sup>12-17</sup>. Even though a detailed theoretical analysis of the hydrodynamics of operation of the detector is also available<sup>5</sup>, the non-linear aspects of the detector have not been fully analyzed. It is the purpose of the present paper to provide a theoretical basis and interpretations for the non-linearities of the detector.

## THEORETICAL ANALYSIS

### *Background and simplified treatment*

The theoretical treatment of the operation that we published earlier<sup>5</sup> form the starting base for the present analysis. It was shown that the relationship between the change in the reference gas flow-rate over the sensing elements (*i.e.*  $\Delta Q$ ) and the physical properties of the gases in the various conduits of the detector and the detector dimensions (as referred to in Fig. 2) is given by eqn. 1.

$$\begin{aligned} \Delta Q &= Q_7 - Q_8 \\ &= (\pi g HR_4^4/8\mu l) \left\{ \frac{(\rho'' - \rho) + (\mu''/\mu') (\rho'/\rho'') [A] [(\rho' - \rho) + P_1/gH] + P_2/gH}{B + C(\mu''/\mu)(\rho/\rho'') + D (\mu''/\mu')(\rho'/\rho'')} \right\} \quad (1) \end{aligned}$$

where  $A = (R_2/R_3)^4 + (l'/h) (R_2/R_4)^4$ ,  $B = 1 + (h/l) (R_4/R_1)^4$ ,  $C = (l'/l) + (h/l) (R_4/R_3)^4$ ,  $D = (R_2/R_3)^4 + (l'/h) (R_2/R_4)^4 + (l'/l) (R_2/R_1)^4 + (h/l) (R_2/R_3)^2$



$$\Delta Q = (\pi g H R_4^4 / 8 \mu l) \left\{ \frac{(\mu/\mu') (\rho'/\rho) [A] (\rho' - \rho)}{1 + (l'/l) + (\mu/\mu') (\rho'/\rho) [A]} \right\} \quad (4)$$

Since for a properly designed detector conforming to the conditions of eqn. 2,  $A \gg 1$  and  $l'/l < 1$ , then at low solute levels, eqn. 4 becomes:

$$\Delta Q = (\pi g H R_4^4 / 8 \mu l) (\rho' - \rho) \quad (5)$$

which is only now linear with the density change ( $\rho' - \rho$ ). Under any other circumstances, changes in viscosity and density (or more appropriately, the changes in the kinematic viscosities, *i.e.*,  $\mu_i/\rho_i$  ratios) will make the response non-linear. The lower limit of concentration of solute, that will start non-linearities in the response, will therefore depend on the kinematic viscosities of the solute, the carrier gas and the reference gas. The greater the difference in the kinematic viscosities, the lower will be the upper limit for linearity.

Eqn. 5 is often taken as the relationship that describes the gas density detector. It assumes linearity between the change in the flow-rate and the change in the density. The experimental verification of this relationship with respect to its range of applicability for any solute is not extensive. In one study<sup>3</sup>, using nitrogen as reference and carrier gas, linear response is reported for acetone, propane and butane, but without information on their upper limit (of concentration) for linearity. One other study<sup>7</sup>, using carbon dioxide as the carrier and reference gas and 3-methylpentane as the solute, reports deviation from linearity after 5- $\mu$ l injection. A later study<sup>18</sup> using sulfur hexafluoride as the reference and carrier gas, reports departure from linearity for methane, nitrogen and carbon dioxide as solutes; upper limits of linearity for these solutes being 40  $\mu$ l, 80  $\mu$ l and 190  $\mu$ l, respectively.

These experimental trends are in accord with the expectations from the non-linear form of the equations in which, as stated earlier, variations in kinematic viscosity is the primary source of non-linearities. Table I is a compilation of the physical properties for some carrier gases and solutes. As shown, kinematic viscosities for sulfur hexafluoride, carbon dioxide, nitrogen and methane increase in that order and therefore when sulfur hexafluoride is used as the carrier gas, methane as a solute will cause the largest change in the kinematic viscosity and therefore the onset of non-linearities may be expected to occur at lower concentrations for methane than for nitrogen or carbon dioxide. The value permissible for carbon dioxide will be the largest. These trends are in fact what is experimentally observed. If, however, nitrogen were the carrier gas, non-linearities would be expected to occur at much higher concentration for methane than for sulfur hexafluoride.

#### GENERAL TREATMENT

For the proper prediction of the response of the detector, appropriate expressions for the densities and viscosities for various gaseous mixtures must be substituted in the more general relationship given by eqn. 3. For ease in interpretations, and also from the stand point of using the detector in molecular weight determinations, it is desirable that these quantities are further related to the molecular weight of the

TABLE I  
PHYSICAL PROPERTIES OF VARIOUS GASES

Gas	Molecular weight ( <i>M</i> )	Critical properties*		Boiling point** <i>T<sub>b</sub></i> (°C)	Density*** × 10 <sup>4</sup> <i>ρ</i> (g/cm <sup>3</sup> )	Viscosity*,** × 10 <sup>6</sup> <i>μ</i> (poise)	Kinematic viscosity <i>μ/ρ</i> (stokes)
		<i>T<sub>c</sub></i> (°K)	<i>P<sub>c</sub></i> (atm)				
He	4	5.19	2.24	-268.9	0.166	194	1.17
N <sub>2</sub>	28	126.2	33.5	-195.8	11.6	178	0.15
CO <sub>2</sub>	44	304.2	72.8	-78.5	18.3	148	0.08
SF <sub>6</sub>	146	318.7	37.1	-63.8	60.7	180 <sup>§</sup>	0.03
C <sub>2</sub> ClF <sub>5</sub> (Freon 115)	154.5	353.2	31.2	-39	64.3	126 <sup>§§</sup>	0.02
CH <sub>4</sub>	16	190.6	45.4	-164	6.6	109	0.17
C <sub>2</sub> H <sub>6</sub>	30	305.4	48.2	-88.6	12.5	90	0.07
C <sub>3</sub> H <sub>8</sub>	44	369.8	41.9	-42.1	18.3	81	0.04
C <sub>4</sub> H <sub>10</sub>	58	425.2	37.5	-0.5	24.1	74	0.03

\* Ref. 19.

\*\* Ref. 20. Viscosities are at 20°C.

\*\*\* Assuming ideal gas behavior, calculated from  $\rho = PM/RT$  at 20°C.

§ Ref. 7.

§§ Estimated using the group contribution approach of Reichenberg described in ref. 19.

constituents. Appropriate expressions for densities and viscosities are now developed below.

#### Densities of the gas mixtures in the various conduits of the detector

For a real gas, the equation of state as power series in density ( $\rho$ ) is given by<sup>21</sup>:

$$Pv/RT = 1 + B\rho + C\rho^2 + \dots \quad (6)$$

where  $P$  is pressure,  $v$  molar volume,  $R$  gas constant,  $T$  is temperature in °K and  $B$ ,  $C$ , etc. are the virial coefficients. If left hand side of this equation is multiplied and divided by the molecular weight of the gas,  $M$ , and if it is realized that  $M/v = \rho$ , the equation becomes

$$PM/RT = \rho + B\rho^2 + C\rho^3 + \dots \quad (7)$$

For an ideal gas, the virial coefficients are zero, and

$$\rho = PM/RT \quad (8)$$

If only the second term in the expansion is retained to describe the behavior of a real gas, then

$$\rho = [(1/4B^2) + PM/BRT]^{1/2} - (1/2B) \quad (9)$$

which is obtained by solving the quadratic equation. Either eqn. 8 or 9 can be used for density determinations. As a first approximation, however, it is reasonable to

assume that under the operational temperatures (*ca.* 200–250°C) and pressures (< 5 atm) in the detector, the gases will behave ideally. From the critical properties ( $T_c$  and  $P_c$ ) given in Table I, it can be seen that at detector temperatures and pressures, relative temperature  $T_r (= T/T_c)$  will be typically greater than 1, and relative pressure  $P_r (= P/P_c)$  will be less than 1. Under such conditions, the compressibility factor  $z (= PV/RT)$  for gases approaches 1, as in ideal gases.

It is therefore reasonable to express the densities for the pure components as follows:

$$\rho_R = (P/RT) M_R (= \rho) \quad (10a)$$

$$\rho_C = (P/RT) M_C \quad (10b)$$

$$\rho_X = (P/RT) M_X \quad (10c)$$

where the subscripts R, C, and X refer to the reference gas, carrier gas, and the solute, respectively.

If the mole (or for ideal gases, equivalently the volume) fraction of the solute in the column effluent gas is  $Y$ , then the density of the column effluent ( $\rho'$ ) can be written as:

$$\rho' = (1 - Y) \rho_C + Y\rho_X \quad (11)$$

or

$$\rho' = (P/RT) [(1 - Y) M_C + YM_X] \quad (12)$$

Since, in eqns. 1–5,  $\rho$  refers to the density of the pure reference gas, the difference ( $\rho' - \rho$ ) becomes:

$$(\rho' - \rho) = (P/RT) [Y(M_X - M_C) + (M_C - M_R)] \quad (13)$$

The density of the gas mixture at the detector exit (*i.e.*,  $\rho''$ ) can be evaluated as follows: Let  $Q_R$  and  $Q_C$  represent the volumetric flow-rates of the reference and the column effluent gases. Let  $Q_E$  be the total (combined) volumetric flow-rate at the detector exit. Let the ratio of the reference to column flow-rate (*i.e.*,  $Q_R/Q_C$ ) be represented by  $q$ . Now, mass balance around the detector requires that:

$$\rho Q_R + \rho' Q_C = \rho'' Q_E \quad (14)$$

or

$$q\rho + \rho' = \rho'' (Q_E/Q_C) \quad (15)$$

Furthermore, since  $Q_E = Q_C + Q_R$ , eqn. 15 becomes

$$q\rho + \rho' = (1 + q) \rho'' \quad (16)$$

or

$$\rho'' = [q/(q + 1)]\rho + [1/(q + 1)]\rho' \quad (17)$$

or by substituting for  $\rho$  and  $\rho'$ , one obtains:

$$\rho'' = \{P/[(q + 1)RT]\} [qM_R + M_C + Y(M_X - M_C)] \quad (18)$$

Therefore, the difference ( $\rho'' - \rho$ ) becomes

$$(\rho'' - \rho) = \{P/[(q + 1)RT]\} [Y(M_X - M_C) + (M_C - M_R)] \quad (19)$$

These relationships can be used to replace the density terms in eqns. 1-5 in terms of the molecular weights of the reference and the carrier gases ( $M_R$  and  $M_C$ ) and the solute ( $M_X$ ); the reference-to-carrier flow ratio ( $q$ ) and the mole fraction ( $Y$ ) of the solute in the column effluent gas.

These derivations have been carried out for the general case where the carrier and the reference gases may be different. When, as is the usual practice, they are the same gases,  $M_R = M_C$ , and simpler relationships are obtained.

It is interesting to note the relative magnitudes of the density differences ( $\rho' - \rho$ ) and ( $\rho'' - \rho$ ). From eqns. 13 and 19

$$(\rho' - \rho) / (\rho'' - \rho) = (q + 1) \quad (20)$$

which clearly indicates that it is only when  $q$  is very large that the contribution from the ( $\rho'' - \rho$ ) term in eqn. 1 may be neglected.

#### *Viscosities of the gas mixtures in the various conduits of the detector*

A common relationship for the viscosity of a pure gas ( $i$ ) is the Chapman-Enskog equation<sup>22</sup>, i.e.,

$$\mu_i = 2.67 \cdot 10^{-5} (M_i T)^{1/2} / (\sigma_i^2 \Omega_i) \quad (21)$$

where  $\sigma$  is the collision diameter ( $\text{\AA}$ ) and  $\Omega$  is the collision integral which depends on the potential energy of interaction. For non-interacting hard spheres,  $\Omega$  is equal to 1. This equation is known to give reasonable estimates of the viscosity (in units of poise) for both monatomic and polyatomic gases. At a given temperature, by combining the terms other than the molecular weight as  $\mu_i^\circ$ , one can write

$$\mu_i = \mu_i^\circ (M_i)^{1/2} \quad (22)$$

which provides a simple relationship between the viscosity and the molecular weight of a gas.

For mixtures, the viscosity can be estimated from

$$\mu_{\text{mix}} = \sum_{i=1}^N \left\{ (y_i \mu_i) / \left( \sum_{j=1}^N y_j \Phi_{ij} \right) \right\} \quad (23)$$

where  $N$  is the number of chemical species in the mixture,  $y_i$  and  $y_j$  are the mole fractions of species  $i$  and  $j$ , and the quantity  $\Phi_{ij}$  is properly given by the Wilke equation<sup>22</sup>, i.e.,

$$\Phi_{ij} = [1 + (\mu_i/\mu_j)^{1/2} (M_j/M_i)^{1/4}]^2 [8(1 + M_i/M_j)]^{-1/2} \quad (24)$$

where  $\mu_i$  and  $\mu_j$  are the viscosities of pure components and  $M_i$  and  $M_j$  are their molecular weights. A less accurate but much simpler expression for  $\Phi_{ij}$  is the Herning and Zipperer approximation<sup>22</sup> according to which

$$\Phi_{ij} = (M_j/M_i)^{1/2} \quad (25)$$

For a binary mixture, eqn. 23 leads to

$$\mu_{\text{mix}} = [y_1\mu_1/(y_1\Phi_{11} + y_2\Phi_{12})] + [y_2\mu_2/(y_1\Phi_{21} + y_2\Phi_{22})] \quad (26)$$

or when combined with eqn. 25

$$\mu_{\text{mix}} = y_1\mu_1/[y_1 + y_2 (M_2/M_1)^{1/2}] + y_2\mu_2/[y_2 + y_1 (M_1/M_2)^{1/2}] \quad (27)$$

Eqns. 22 and 27 can be used to express the viscosities of the gases in the various conduits of the detector.

In eqns. 1-4,  $\mu$  represents the viscosity of the reference gas and will be expressed as

$$\mu = \mu_R^\circ (M_R)^{1/2} \quad (28)$$

The column effluent gas is a mixture of the pure carrier gas (of molecular weight  $M_C$  and viscosity  $\mu_C$ ) and the solute (of molecular weight  $M_X$  and viscosity  $\mu_X$ ). The viscosity ( $\mu'$ ) of the column effluent can therefore be written as

$$\mu' = \{Y\mu_X^\circ (M_X)^{1/2}/[Y + (1 - Y) (M_C/M_X)^{1/2}]\} + \{(1 - Y) \mu_C^\circ (M_C)^{1/2}/[(1 - Y) + Y(M_X/M_C)^{1/2}]\} \quad (29)$$

or

$$\mu' = [Y \mu_X^\circ M_X + (1 - Y) \mu_C^\circ M_C]/[Y(M_X)^{1/2} + (1 - Y) (M_C)^{1/2}] \quad (30)$$

The gas leaving the detector is a mixture of the column effluent and the reference gas and its viscosity ( $\mu''$ ) can be written as:

$$\mu'' = \{Z \mu_{\text{CE}}^\circ (M_{\text{CE}})^{1/2}/[Z + [1 - Z) (M_R/M_{\text{CE}})^{1/2}]\} + \{(1 - Z) \mu_R^\circ (M_R)^{1/2}/[(1 - Z) + Z(M_{\text{CE}}/M_R)^{1/2}]\} \quad (31)$$

where CE refers to column effluent and  $Z$  is the mole (or volume) fraction of the column effluent in the combined exit flow, that is,

$$Z = Q_C/Q_E \quad (32)$$



Since  $Q_E = Q_R + Q_C$  and  $Q_R/Q_C = q$ ,  $Z$  can be expressed in terms of  $q$  as:

$$Z = 1/(1 + q) \quad (33)$$

Therefore, by combining eqns. 31 and 33,

$$\mu'' = [\mu_{CE}^\circ M_{CE} + q \mu_R^\circ M_R] / [(M_{CE})^{1/2} + q(M_R)^{1/2}] \quad (34)$$

And, since molecular weight of the column effluent is given by  $M_{CE} = (1 - Y) M_C + Y M_X$  viscosity of the gas exiting the detector becomes

$$\mu'' = \{ \mu_{CE}^\circ [M_C + Y(M_X - M_C)] + q \mu_R^\circ M_R \} / \{ [M_C + Y(M_X - M_C)]^{1/2} + q [M_R]^{1/2} \} \quad (35)$$

where  $Y$  again refers to the mole fraction of the solute in the column effluent, and  $q$  is the reference-to-carrier flow ratio.

It should be noted that when the reference and the carrier gases are the same, equations will be simpler since  $M_R = M_C$  and  $\mu_R^\circ = \mu_C^\circ$  and as a first approximation  $\mu_{CE}^\circ \cong \mu_R^\circ$  may be assumed. When  $Y = 0$ , eqn. 35 then reduces to  $\mu'' = \mu_R^\circ (M_R)^{1/2} = \mu_R$ , as it should. These expressions for  $\mu$ ,  $\mu'$ , and  $\mu''$  can now be substituted for viscosities in the general equations describing the detector response.

#### Detector response

The electrical response from the detector is given by

$$E = k \Delta Q \quad (36)$$

where  $k$  is a proportionality constant and  $\Delta Q$  is given by eqn. 1. When the carrier and the reference gases are the same,  $M_C = M_R$  and  $\mu_{CE}^\circ \cong \mu_C^\circ$ , and therefore,

$$(\rho'' - \rho) = [P/RT (q + 1)] Y [M_X - M_C] \quad (37)$$

$$(\rho' - \rho) = (P/RT) Y [M_X - M_C] \quad (38)$$

$$(\mu''/\mu')(\rho'/\rho'') = \frac{(q+1)[(1-Y)M_C + YM_X][Y(M_X)^{1/2} + (1-Y)(M_C)^{1/2}]}{[(1-Y)M_C + (\mu_X^\circ/\mu_C^\circ)YM_X][(M_C(1-Y) + YM_X)^{1/2} + q(M_C)^{1/2}]}, \quad (39)$$

$$(\mu''/\mu)(\rho/\rho'') = [(q + 1) (M_C)^{1/2}] / \{ [M_C (1 - Y) + M_X Y]^{1/2} + q (M_C)^{1/2} \} \quad (40)$$

Combining eqns. 37-40 with eqn. 1, a general relationship (eqn. 41) for detector response, that involves the detector dimensions, molecular weights of the carrier gases and the solute, the reference-to-carrier flow ratio, the mole fraction (or amount) of solute in the column effluent, and the pressure losses at elbows and T-joints as the parameters, is obtained. Except for the pressure loss terms, the other parameters can be varied at will and their effects on the detector response can be analyzed.

$$E = k' \left\{ \frac{[Y(M_X - M_C) + P_2] + \{[Y(M_X - M_C) + P_1] A(q + 1)^2 \frac{M_C + Y(M_X - M_C)}{M_C + Y\left(\frac{\mu_X^\circ}{\mu_C^\circ} M_X - M_C\right)} \left\{ \frac{(M_C)^{1/2} + Y[(M_X)^{1/2} - (M_C)^{1/2}]}{[M_C + Y(M_X - M_C)]^{1/2} + q(M_C)^{1/2}} \right\}}}{B(q + 1) + \left\{ \frac{C(q + 1)^2 (M_C)^{1/2}}{[M_C + Y(M_X - M_C)]^{1/2} + q(M_C)^{1/2}} \right\} + \{D(q + 1)^2 \frac{M_C + Y(M_X - M_C)}{M_C + Y\left(\frac{\mu_X^\circ}{\mu_C^\circ} M_X - M_C\right)} \left\{ \frac{(M_C)^{1/2} + Y[(M_X)^{1/2} - (M_C)^{1/2}]}{[M_C + Y(M_X - M_C)]^{1/2} + q(M_C)^{1/2}} \right\}} \right\} \quad (41)$$

where  $k' = k\pi gHR_d^2 P / (8\mu lRT)$ ,  $P_2 = P_2 RT / (gHP)$  and  $P_1 = P_1 RT / (gHP)$ .

## DISCUSSIONS

The highly non-linear nature of eqn. 41 is evident and arises from the terms involving  $(\mu''/\mu')$  ( $\rho'/\rho''$ ) and  $(\mu''/\mu)$  ( $\rho/\rho''$ ).

It is interesting to note that these terms will behave as constants and their non-linear effects will not be observed if the following conditions are satisfied.

$$(1) Y [M_X - M_C] \ll M_C \quad (42a)$$

$$(2) Y [(M_X)^{1/2} - (M_C)^{1/2}] \ll M_C \quad (42b)$$

$$(3) Y [(\mu_X^\circ/\mu_C^\circ) M_X - M_C] \ll M_C \quad (42c)$$

$$(4) [M_C + Y(M_X - M_C)]^{1/2} \ll q(M_C)^{1/2} \quad (42d)$$

Under such conditions from eqn. 31,

$$(\mu''/\mu') (\rho'/\rho'') = (q + 1)/q \quad (43a)$$

and from eqn. 40

$$(\mu''/\mu) (\rho/\rho'') = (q + 1)/q \quad (43b)$$

and eqn. 41 becomes

$$E = \frac{k' \{ Y(M_X - M_C)[q + A(q + 1)^2] + qP_2 + A(q + 1)^2 P_1 \}}{\{ B(q + 1)q + [C + D](q + 1)^2 \}} \quad (44)$$

which, for a given reference-to-carrier flow ratio  $q$ , is linear. (Provided that the pressure loss terms will have a fixed value once the flow conditions are specified).

It is clear that at low solute contents, *i.e.*, as  $Y \rightarrow 0$ , all the conditions of eqn.

42 are satisfied. However, at high solute levels, and as a limiting case, as  $Y \rightarrow 1.0$ , these requirements become:

$$(1) M_X \ll 2M_C \quad (45a)$$

$$(2) (M_X)^{1/2} \ll 2(M_C)^{1/2} \text{ or } M_X \ll 4M_C \quad (45b)$$

$$(3) M_X \ll (\mu_C^\circ/\mu_X^\circ) M_C \quad (45c)$$

$$(4) M_X \ll q^2 M_C \quad (45d)$$

Comparison of the requirements 1 and 4 suggests that the ratio of the reference-to-carrier flow,  $q$ , should be chosen to be at least equal to or greater than 1.41. It is clear from condition 4 that when using a low-molecular-weight carrier, for improved linearity  $q$  should be set higher than that for a high molecular weight carrier. For example,  $q$  for helium should be much higher than that for nitrogen, carbon dioxide or sulfur hexafluoride, the lowest value being permissible with sulfur hexafluoride. Table II shows the variation of the critical values of  $q$  that would be required with various carrier gases for solutes at different molecular weights in order to satisfy the condition  $M_X \ll q^2 M_C$ . Actual reference-to-carrier flow ratios should be greater than these values. Optimum  $q$  values are however a compromise between linearity and maximum sensitivity. Relative magnitudes of  $q$  values shown in Table II are in agreement with the trends in  $q$  values that are experimentally determined to be optimum for various carrier gases<sup>6,7</sup>. For example, using 3-methylpentane as solute, at a carrier flow-rate of 2 l/h, optimum  $q$  values for sulfur hexafluoride, carbon dioxide and nitrogen were about 0.6, 1.5, and 3 respectively<sup>7</sup>. Since the molecular weight of 3-methylpentane is 86, the present analysis would have predicted the values to be at least 0.77, 1.4, and 1.75 respectively.

It is clear from eqns. 42 and 45 that at any given concentration of solute, the linearity of the response is dependent on the molecular weight of the solute and can be improved by selecting higher-molecular-weight carrier gases. Another factor which favors linearity is the selection of a large value for the ratio of reference-to-carrier-

TABLE II  
CRITICAL VALUES OF REFERENCE-TO-CARRIER FLOW RATIO ( $q$ ) FOR DIFFERENT CARRIER GASES FOR DIFFERENT SOLUTES

Solute $M_X$	Reference-to-carrier flow ratio			
	He	N <sub>2</sub>	CO <sub>2</sub>	SF <sub>6</sub>
50	3.53	1.33	1.06	0.58
100	5.0	1.89	1.50	0.83
150	6.12	2.31	1.85	1.01
200	7.07	2.67	2.13	1.17
250	7.90	2.98	2.38	1.31
300	8.66	3.27	2.61	1.43
400	10.0	3.78	3.01	1.65

TABLE III  
LENNARD JONES POTENTIAL PARAMETERS FOR VISCOSITY DETERMINATIONS<sup>23,24</sup>

Substance	$M_X$	$\sigma$ ( $^{\circ}A$ )	$\epsilon/k$ ( $^{\circ}K$ )	$T = 300^{\circ}K$		$T = 500^{\circ}K$	
				$kT/\epsilon$	$\Omega$	$kT/\epsilon$	$\Omega$
He	4	2.551	10.22	29.4	0.7	48.9	0.65
N <sub>2</sub>	28	3.798	71.4	4.2	0.96	7.0	0.87
CO <sub>2</sub>	44	3.941	195.2	1.54	1.3	2.56	1.08
SF <sub>6</sub>	146	5.128	222.1	1.35	1.375	2.25	1.13
CH <sub>4</sub>	16	3.758	148.6	2.01	1.175	3.36	1.0
C <sub>8</sub> H <sub>18</sub>	114	7.45	320	0.94	1.63	1.56	1.28

gas flow rates. However, the magnitude of  $\mu_C^{\circ}/\mu_X^{\circ}$  in requirement 3 (eqns. 42 and 45) is not easy to see without some calculations. From eqns. 21 and 24, this ratio becomes

$$(\mu_C^{\circ}/\mu_X^{\circ}) = (\sigma_X/\sigma_C)^2 (\Omega_X/\Omega_C) \quad (46)$$

Since the collision integrals ( $\Omega$ ) are temperature dependent, the magnitudes of  $\mu_C^{\circ}/\mu_X^{\circ}$  will be assessed at different temperatures. Table III gives the values of the hard sphere diameters ( $\sigma$ ) and collision integrals at 300°K and also 500°K for some carrier gases and solutes. Temperature dependence is observed to be not too large. For methane and octane as solutes and helium, nitrogen, carbon dioxide and sulfur hexafluoride as carrier gases the values of  $\mu_C^{\circ}/\mu_X^{\circ}$  at 500°C are given below:

Solute	Carrier Gas			
	He	N <sub>2</sub>	CO <sub>2</sub>	SF <sub>6</sub>
CH <sub>4</sub>	3.34	1.13	0.84	0.47
C <sub>8</sub> H <sub>18</sub>	16.8	5.66	4.23	2.39

It is clear from these calculations that when using higher-molecular-weight carrier gases such as carbon dioxide or sulfur hexafluoride,  $\mu_C^{\circ}/\mu_X^{\circ}$  ratio for some low-molecular-weight solutes becomes less than 1, otherwise the ratio is greater than 1. Since the condition of this ratio being less than 1 occurs with high-molecular-weight carrier and low-molecular-weight solute combinations, the third requirements in eqns. 42 or 45 do not introduce any more strict limitations on the molecular weight range of the solutes to maintain linearity in the detector response. Based on these analyses, linear response can in principle be expected as long as  $M_X \ll 2M_C$  over all practical ranges of concentrations that may be encountered in gas chromatographic analyses.

For a given solute of molecular weight  $M_X$ , the upper limit of linearity can be also expressed in terms of the sample size in the carrier gas. For linear response, at a given mole fraction  $Y$  of solute, the requirements of eqn. 42 become:

$$(1) Y \ll M_C/(M_X - M_C) \quad (47a)$$

$$(2) Y \ll M_C / [(M_X)^{1/2} - (M_C)^{1/2}] \quad (47b)$$

$$(3) Y \ll M_C / [(\mu_X^\circ / \mu_C^\circ) M_X - M_C] \quad (47c)$$

$$(4) Y \ll (q^2 - 1) M_C / (M_X - M_C) \quad (47d)$$

These equations show clearly that the upper limit of linearity (or maximum concentration for which detector response will be linear) is inversely proportional to the difference between molecular weights of the sample and the carrier. As indicated earlier, the upper limits of linearity for methane, nitrogen and carbon dioxide in a system using sulfur hexafluoride as carrier have been reported to be 40  $\mu$ l, 80  $\mu$ l, and 190  $\mu$ l respectively<sup>18</sup>. Based on these experimental values, the authors<sup>18</sup> had noted (without explanations) that the maximum gas concentration for which the detector response was linear was inversely proportional to the molecular weight differences between the carrier and the solute. The present analysis provides an explanation either in terms of the kinematic viscosities (see the section on Background and simplified treatment) or through eqns. 47 a-d which are derived from kinematic viscosities but involve the molecular weights in an explicit manner.

Experimental data available in the literature<sup>6,7</sup> show a dependence of the detector response on the reference-to-carrier flow ratio  $q$  also. The response passes through a maximum as  $q$  is increased, and the value of  $q$  corresponding to this maximum response depends on the nature of the carrier gas. Furthermore, at a given  $q$  as the carrier gas flow-rate is increased, response becomes smaller and the location of the maximum shifts to a lower value of  $q$ . As discussed below, the present development accounts for most of these trends as well.

It should be noted that the general relationship (*i.e.*, eqn. 41) and the more restricted form (eqn. 44) both involve the reference-to-carrier flow ratio  $q$  as a parameter in an explicit manner. Variation of the response with  $q$  and the location of maximum  $q$  can be analyzed by differentiating  $E$  with respect to  $q$  and setting  $dE/dq = 0$ . However, before proceeding any further, it should be realized that the magnitudes of the terms that account for pressure losses at elbows and T-joints will depend on the flow-rates, and this dependence must be incorporated into the equations.

$P_1$  that appears in eqn. 1 refers to the following sum of pressure drops<sup>5</sup> (see Fig. 2).

$$P_1 = (P_B - P_C) + (P_O - P_S) + (P_T - P_U) + (P_Y - P_N) + (P_B - P_P) + (P_R - P_A) \quad (48)$$

Since first and fifth terms will be of the same order of magnitude but opposite in sign, and similarly for second and fourth terms,  $P_1$  can be approximated as

$$P_1 \cong (P_T - P_U) + (P_R - P_A) \quad (49)$$

which represent the pressure losses at the entrance of carrier and reference gases to the vertical conduits.

The term  $P_2$  refers to the sum

$$P_2 = P_1 + (P_S - P_F) + (P_G - P_H) + (P_I - P_J) + (P_K - P_L) + (P_M - P_V) + (P_U - P_T) \quad (50)$$

By making the approximation that the second and sixth terms and third and the fifth terms will cancel each other,

$$P_2 = P_1 + (P_I - P_J) + (P_U - P_T) \quad (51a)$$

or, substituting for  $P_1$  from eqn. 49

$$\begin{aligned} P_2 &\cong (P_T - P_U) + (P_R - P_A) + (P_I - P_J) + (P_U - P_T) \\ &= (P_R - P_A) + (P_I - P_J) \end{aligned} \quad (51b)$$

which now represent the pressure losses at the entrance of the reference gas and at the exit of the combined gases from the detector.

Pressure losses in fittings and valves are typically given by a relationship of the form

$$\Delta P = K_f \rho V^2 / 2 = K_f \rho Q^2 / (2\pi^2 R^4) \quad (52)$$

where  $\rho$  is the density,  $V$  represents linear velocity,  $Q$  volumetric flow-rate, and  $K_f$  is a factor that depends on the nature of the fitting and the Reynolds number for the flow conditions. Since the terms involved in eqns. 49 and 52 involve T-joints,  $K_f$  should be chosen accordingly. The values of  $K_f$  for T-joints are given below for different Reynolds numbers ( $N_{Re}$ )<sup>25</sup>.

	$N_{Re}$				
	> 2100	1000	500	100	50
$K_f$ , branch to line	1.0	1.5	1.8	4.9	9.3
$K_f$ , along run	1.0	0.4	0.5	2.5	—

Flow conditions in the conduits of the detector are typically laminar<sup>5</sup>, *i.e.*,  $N_{Re} < 2100$ , and it is important to note that as the  $N_{Re}$  becomes smaller, magnitude of  $K_f$  increases and thus the pressure loss terms become more significant.

From combining eqns. 49 and 52,

$$P_1 = [K_f \rho Q_R^2 / (2\pi^2 R_1^4)] + [K_f \rho' Q_C^2 / (2\pi^2 R_2^4)] \quad (53)$$

$$= (K_f Q_C^2 / 2\pi^2) [(\rho q^2 / R_1^4) + (\rho' / R_2^4)] \quad (54)$$

Similarly from eqns. 51 and 52

$$P_2 = [K_f \rho Q_R^2 / (2\pi^2 R_1^4)] + [K_f \rho'' (Q_C + Q_R)^2 / (2\pi^2 R_3^4)] \quad (55)$$

$$= (K_f Q_C^2 / 2\pi^2) [(\rho q^2 / R_1^4) + (\rho'' (1 + q)^2 / R_3^4)] \quad (56)$$

Substitution for  $\rho$ ,  $\rho'$  and  $\rho''$  from eqns. 10, 12, and 18,

$$P_1 = [K_f Q_C^2 P / 2\pi^2 R_1^4 RT] \{M_C [q^2 + (R_1/R_2)^4] + Y (R_1/R_2)^4 [M_X - M_C]\}$$

$$P_2 = [K_f Q_C^2 P / (2\pi^2 R_1^4 RT)] \{M_C [q^2 + \quad (57)$$

$$(1 + q)^2 (R_1/R_3)^4] + Y (R_1/R_3)^4 (1 + q) [M_X - M_C]\} \quad (58)$$

$P_1'$  and  $P_2''$  that appear in eqns. 41 and 44 are obtained by dividing  $P_1$  and  $P_2$  above by  $(gHP/RT)$  and when substituted in eqn. 44, one obtains

$$E = k' \{Y(M_X - M_C)[q + A(q + 1)^2 + q(q + 1)(R_1/R_3)^4 K^* + A(q + 1)^2 (R_1/R_2)^4 K^*] K^* M_C [q^3 + q(1 + q)^2 (R_1/R_3)^4 + A(q + 1)^2 (q^2 + (R_1/R_2)^4)]\} \{Bq(q + 1) + (C + D)(q + 1)^2\}^{-1/2} \quad (59)$$

where  $K^* = K_f Q_C^2 / (2\pi^2 R_1^4 gH)$ .

Since, for the case of no solute entering the detector, (*i.e.*,  $Y = 0$ ), detector bridge is adjusted to give zero response, in elucidating the effect of the changing value of  $q$  on the response, one should consider only the first term in the numerator of eqn. 59. The second term involving  $K^* M_C$  will only result in a shift of the zero point as  $q$  and or  $Q_C$  are changed. Thus the response becomes

$$E' = \frac{k' Y (M_X - M_C) \{q[1 + (1 + q)(R_1/R_3)^4 K^*] + A(q + 1)^2 [1 + (R_1/R_2)^4 K^*]\}}{\{B(q + 1)q + (C + D)(q + 1)^2\}} \quad (60)$$

where  $E'$  is the response that incorporates the zero point shift arising from the readjustment of the flow-rates. Some calculations on the order of magnitude of the terms involving  $K^*$  is instructive at this stage. The dimensions that are reported<sup>3</sup> for a gas density detector are  $R_1 = 15$  mm;  $R_2 = 4$  mm;  $R_3 = 2$  mm;  $l' = 10$  mm;  $l = 15$  mm;  $h = 50$  mm; and  $H = 100$  mm. As discussed earlier  $K_f$  values in laminar flow conditions are typically in the range 1 to 5. Assuming a value  $K_f = 2$ , at a column flow-rate of 2 l/h, the quantity  $K^*$  (which is dimensionless) becomes  $1.9 \cdot 10^{-6}$ . Therefore,  $(R_1/R_3)^4 K^* = 3.75 \cdot 10^{-4}$  and  $(R_1/R_2)^4 K^* = 6 \cdot 10^{-3}$  which are both very small compared to 1, and can be neglected. Thus, eqn. 60 becomes:

$$E' = k' Y (M_X - M_C) [q + A(q + 1)^2] / [B(q + 1)q + (C + D)(q + 1)^2] \quad (61)$$

This equation can be rearranged into a form

$$E' = k' Y [M_X - M_C] \{[\alpha q^2 + \beta q + \gamma] / [\alpha' q^2 + \beta' q + \gamma']\} \quad (62)$$

where

$$\begin{aligned}\alpha &= A; \beta = 1 + 2A; \gamma = A; \text{ and } \alpha' = B + C + D; \\ \beta' &= B + 2(C + D); \gamma' = C + D\end{aligned}\quad (63)$$

The condition  $dE'/dq = 0$  requires that

$$(\alpha\beta' - \beta\alpha')q^2 + 2(\alpha\gamma' - \alpha'\gamma)q + (\beta\gamma' - \beta'\gamma) = 0 \quad (64)$$

and thus the value of  $q$  which will lead to an extremum in response becomes

$$q = \{(\alpha'\gamma - \alpha\gamma') \mp [(\alpha\gamma' - \alpha'\gamma)^2 - (\beta\gamma' - \beta'\gamma)(\alpha\beta' - \beta\alpha')]\}^{1/2} / (\alpha\beta' - \beta\alpha') \quad (65)$$

From physical considerations,  $q$  has to be positive and real. If the detector dimensions given earlier are substituted into the relationships given in connection with eqn. 1, the parameters  $A$ ,  $B$ ,  $C$ , and  $D$  become;  $A = 19$ ;  $B = 1$ ;  $C = 4$ ; and  $D = 19$ . Using these values, from eqns. 63 and 65,  $q_{\max}$  is calculated to be 0.095. At values greater than 0.095, for the detector with these specified dimensions, response shows a decrease. The maximum is very shallow however. It is easy to see from eqn. 62 that when  $q = 0$ , the quantity in the large parenthesis becomes  $\gamma/\gamma'$  and as  $q$  becomes very large approaches  $\alpha/\alpha'$ . With the given numerical values, the magnitude of this factor changes (increases) from 0.8261 (at  $q = 0$ ) to 0.8264 (at  $q = 0.095$ ) and eventually decreases to 0.7917 (as  $q \rightarrow \infty$ ). It is to be noted, however, that the range of these values and the nature (*i.e.*, sharpness) of the maximum in the response as a function of  $q$  is very much dependent upon the dimensions of the detector which determine the quantities  $A$ ,  $B$ ,  $C$ , and  $D$ .

It should be noted that the value of  $q_{\max}$  predicted from eqns. 62-65 shows no dependence on the type of the carrier gas and the magnitude of the carrier flow-rate. Therefore, based on this analysis, it may be concluded that for a detector displaying linear response behavior (describable by eqn. 62 for example), the value of  $q_{\max}$  corresponding to the maximum in response is expected to be independent of the carrier type.

As mentioned earlier, experimental data reported in the literature<sup>6,7</sup> indicates a dependence of  $q_{\max}$  on the carrier type. For example at a carrier flow-rate of 2 l/h, using 1- $\mu$ l injections of 3-methylpentane, the maximum response from a detector operated at 115°C, occurs at about  $q = 0.6$  for sulfur hexafluoride,  $q = 1.5$  for carbon dioxide and  $q = 3$  for nitrogen and argon. Except for sulfur hexafluoride, the maximum is not a sharp one. Furthermore, as the carrier flow-rate is increased, the location of  $q_{\max}$  shifts to values less than 1 for all these gases and the maximum become less pronounced. The physical effect of increasing the flow-rate of the carrier while holding the injected amount of the solute unchanged is in a way to decrease the mole fraction of the solute ( $Y$ ) in the carrier gas, which should favor the linear response behavior of the detector. In this respect, the experiments and the observations from the analysis of eqn. 62 appear to be in agreement. Increasing the magnitude of  $Y$  has a direct effect on the magnitude of the response also (see eqn. 62) and therefore it is not surprising to see that the magnitude of the response rapidly decreases as the carrier flow-rates are increased.



Dependence of the variation of response with the reference-to-flow ratio  $q$  on the type of the carrier gas is present, however, if the analysis is based on the general non-linear relationship, *i.e.*, eqn. 41 instead of the linear form, eqn. 62. Assuming here also that the effects of the pressure loss terms ( $P_1'$  and  $P_2'$ ) are taken into account by the zero point shift adjustment, it is possible to rearrange eqn. 41 into a form which is identical with eqn. 62 with a solution for  $q_{\max}$  given by eqn. 65. However, for this non linear case, the quantities  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\alpha'$ ,  $\beta'$ , and  $\gamma'$  are given by the following equations.

$$\alpha = A[M_C + Y(M_X - M_C)] \{(M_C)^{1/2} + Y[(M_X)^{1/2} - (M_C)^{1/2}]\} / \{M_C + Y[(\mu_X^\circ/\mu_C^\circ)M_X - M_C]\} \quad (66a)$$

$$\beta = 2\alpha + (M_C)^{1/2} \quad (66b)$$

$$\gamma = \alpha + [M_C + Y(M_X - M_C)]^{1/2} \quad (66c)$$

$$\alpha' = (B + C) (M_C)^{1/2} + \alpha(D/A) \quad (66d)$$

$$\beta' = (B + 2C) (M_C)^{1/2} + 2\alpha(D/A) + B [M_C + Y(M_X - M_C)]^{1/2} \quad (66e)$$

$$\gamma' = B [M_C + Y(M_X - M_C)]^{1/2} + C (M_C)^{1/2} + \alpha(D/A) \quad (66f)$$

Since these parameters now depend on not only the detector dimensions, but also on  $M_C$ ,  $M_X$  and  $Y$ ,  $q_{\max}$  that will be calculated from eqn. 65 will depend on the type and the flow-rate of the carrier gas, the solute and the amount that is injected. There is no experimental data on the behavior of the system with different solutes. This prediction that there may be a dependence on the type of the solute on the location of  $q_{\max}$  needs to be experimentally examined.

An attempt was made to predict the value of  $q_{\max}$  for 3-methylpentane ( $\rho = 0.664 \text{ g/cm}^3$ ,  $M_X = 86.18$ ) as the solute. Based on the dimensions mentioned earlier, assuming a 10-sec response time for the detector, a 1- $\mu\text{l}$  liquid injection is estimated to correspond to a value of  $Y = 0.04$  (at the detector temperature of 115°C) when the carrier flow-rate is 2 l/h. Using the quantities  $\sigma = 5.9A^\circ$  and  $e/k = 413^\circ\text{K}$  for *n*-hexane as an approximation for 3-methylpentane and for the carrier gases using the properties given in Table III, the ratios  $\mu_X^\circ/\mu_C^\circ$  are calculated to be 0.57, 0.32, and 0.23 for the solute and sulfur hexafluoride, carbon dioxide and nitrogen as the carriers, respectively at 115°C (388°K). Substituting these values into the expressions given in eqn. 66, and solving for  $q_{\max}$  from eqn. 65, however, results in negative values for these carrier gases. A negative value for the reference-to-carrier flow ratio is of course physically not acceptable. The implication is that for  $q \geq 0$ , response should display a decrease as  $q$  increases. This is in contradiction with the experimental results that have been reported. A possible reason may be that the detector dimensions that have been used in the present calculations may not represent the dimensions of the detector with which the reported experimental data were collected. This could explain the very shallow nature of the predicted decrease in response also.

## CONCLUDING REMARKS

The theory that has been developed provides an explanation for almost all the trends that are experimentally observed with the gas density detectors. New set of experimentation with a detector of known dimensions and using various solutes at different injection levels is needed however for a complete test of the theory. A gas density detector that conforms to the dimensions suggested by the theory for increased response and improved linear range would be especially instructive.

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