



Fig. 4. Mass diffusivity, D_{CO, N_2} , calculated by experimental viscosity data with Equation (6) (continuous curve). The circles refer to experimental mass diffusivity values (2).

$$q = q_{Hg} = -\frac{S}{2} \frac{dh}{dt} \quad (15)$$

with t = time and $S = S_0/\cos\theta$. S is the instantaneous area of the interface mercury-gas (see Figure 3). By combining Equations (14) and (15) we get:

$$a \frac{S^2}{4} \left(\frac{dh}{dt} \right)^2 - \frac{S}{2} (d + d_{Hg}) \left(\frac{dh}{dt} \right) - ch = 0 \quad (16)$$

$$a = \frac{\beta \rho}{\pi^2 r^4}; \quad d = \frac{8\eta L}{\pi r^4}; \quad d_{Hg} = \frac{8\eta_{Hg} L_{Hg}}{\pi r_{Hg}^4}; \quad c = g(\rho_{Hg} - \rho) \quad (17)$$

Under the condition $(dh/dt) < 0$, the solution of Equation (16) is given by the negative root:

$$\frac{dh}{dt} \frac{d + d_{Hg}}{a S} [1 - (1 + \gamma h)^{1/2}] \quad (18)$$

$$\gamma = \frac{4 a c}{(d + d_{Hg})^2} \quad (19)$$

The integral of Equation (18) supplies time \bar{t} required for displacing the gas through the capillary:

$$\bar{t} = \frac{S(d + d_{Hg})}{4 a} \left\{ \ln \frac{h_2}{h_1} + 2[(1 + \gamma h_1)^{1/2} - (1 + \gamma h_2)^{1/2}] + \ln \frac{[(1 + \gamma h_2)^{1/2} + 1][(1 + \gamma h_1)^{1/2} - 1]}{[(1 + \gamma h_2)^{1/2} - 1][(1 + \gamma h_1)^{1/2} + 1]} \right\} \quad (20)$$

h_1 and h_2 being the h values at the beginning and the end of the run, respectively.

In Equation (20) the terms S , d_{Hg} , h_1 and h_2 are known instrument constants. d and γ depend on the viscosity, η . By putting measured time \bar{t} , Equation (20) is iteratively solved until a satisfactory value of η is found.

Now, we verify the two main assumptions behind Equation (20). The first is that the gas flow through the capillary is laminar. Equations (14) and (15) have been combined and solved with respect to the gas velocity. This leads to the following expressions for the Reynolds number:

$$N_{Re} = \left[\frac{64 r^6}{\beta^2} \left(\frac{L}{r^4} + \frac{\eta_{Hg} L_{Hg}}{\eta r_{Hg}^4} \right)^2 \right]$$

$$+ \frac{4 r^2 g}{\beta \eta^2} \rho h_1 (\rho_{Hg} - \rho) \left]^{1/2} - \frac{8 r^3}{\beta} \left(\frac{L}{r^4} + \frac{\eta_{Hg} L_{Hg}}{\eta r_{Hg}^4} \right) \quad (21)$$

By Equation (21), the flow appears to be laminar when the instrument operates at the inclination 1 (see Table 5 and Figure 3). For the other inclinations it proved reliable to put into Equation (21) the value of t measured by the instrument at inclination 1 and to verify that the Reynolds number satisfies the condition $N_{Re} \leq 1,500$.

The second assumption behind Equation (20) is that the effective displaced volume of gas, V_{eff} , is equal to that $V = \epsilon S$ of mercury. It implies that $\Delta P \ll P$. To this aim, we consider the instantaneous pressures, P_1^m and P_2^m , in reservoir b at the beginning and at the end of the run:

$$P_1^m = P + g h_1 (\rho_{Hg} - \rho) \frac{V_{II}}{(V_I + V) + V_{II}}; \quad P_2^m = P + g h_2 (\rho_{Hg} - \rho) \frac{V + V_{II}}{(V_I + V) + V_{II}} \quad (22)$$

$(V_I + V)$ and V_{II} indicate the gas volumes at the beginning of the run in reservoirs b and a, respectively. Since the mean pressure is P , the effective displaced volume of gas, V_{eff} , is given by:

$$V_{eff} P = (V_I + V) P_1^m + V_I P_2^m \quad (23)$$

By combining Equations (22) and (23), we get

$$\frac{V_{eff}}{V} = 1 + \frac{\delta}{P} \quad (24)$$

$$\delta = g h_1 (\rho_{Hg} - \rho) \frac{V_{II}(V_I + V) - V_I (V + V_{II}) (h_2/h_1)}{V(V + V_I + V_{II})} \quad (25)$$

the factor δ varying from 0.1129 atm. at the first inclination to 0.2551 atm. at the last inclination of the instrument. By Equation (25), in the range $P > 50$ atm., the ratio δ/P becomes $\leq 10^{-3}$ and the assumption $V_{eff} \approx V$ is fulfilled. In the range $P \leq 50$ atm., where the above assumption is satisfied only within some units percentage, Equation (20) has been corrected, by substituting the measured time, \bar{t} , with time t^* empirically formulated by:

$$t^* = \frac{\bar{t}}{1 + \delta/P} \quad (26)$$

Equation (26) derives from the fact that, when $V_{eff}/V \leq 1.05$, as is the case with $P \leq 50$ atm., the time required for displacing the gas is linearly proportional to the effective displaced volume.

CONCLUSION

In the pressure range up to 900 atm. our viscometer allows viscosity measurements with an accuracy 1%. Within this figure our data on nitrogen agree with those reported by Michels (18).

For the components carbon monoxide and nitrogen at 50°C., Enskog's theory satisfactorily predicts the behavior of the viscosity, whereas beyond 200 atm. is supplemented by P.V.T. measurements. The latter have been carried out with accuracy 1/1,000, which appears to be satisfactory for the present purpose.

The molecular similarity between carbon monoxide and nitrogen enables application of Enskog's theory in order to check the binary mass diffusivity data by those on viscosity.

NOTATION

b_0 ; b = second virial coefficient for a hard spheres gas and for a real gas, respectively