Theory for the Determination of Vapour Pressures by the Transpiration Method

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Equations valid for coupled diffusion and viscous flow are applied to the case of the transpiration experiment. The results presented in this paper do not assume a uniform total pressure in the apparatus, in contrast with the theory developed by Merten. A theory is presented for the diffusion of the sample vapour in opposition to the flow of carrier gas in the carrier gas entrance. Results from this theory are compared with those of Merten.

Recommendations for users of the transpiration method are given.

The transpiration method is one of the simplest and most versatile methods for vapour pressure determinations at high temperatures.[1-3] The apparatus is simple and is shown schematically in Fig. 1. In principle, a carrier gas, which

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may be inert or reactive, is passed over or through the condensed sample under investigation in a constant temperature zone and with a constant flow rate of carrier gas. The flow is desired to be sufficiently slow so that the carrier gas is saturated with the vapour, which is condensed at some point "downstream" from the sample. The vapour pressure may be found by determination of the mass of vapour carried away by a known volume of carrier gas in a known time period, provided the molecular weight of the vapour is known. Conversely, when the molecular weight of the vapour is not known, it may be evaluated from observations by the transpiration method in combination with vapour pressure measurements by some other method. Thus, the transpiration method represents a valuable adjunct to the "boiling point" method, the theory of which is discussed in a subsequent paper.[4] Although
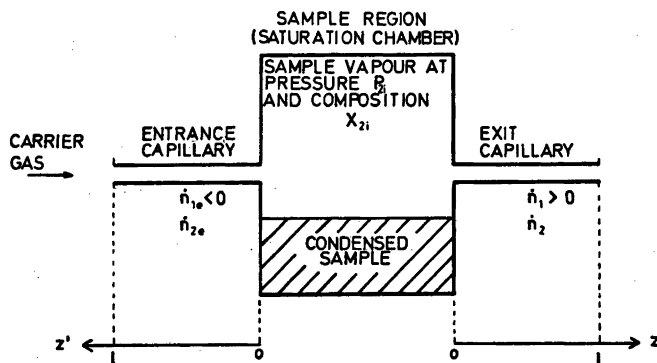

Fig. 1. Schematic diagram of the isothermal part of the apparatus used in a transpiration experiment.

experimentally quite different, the theories of these two methods have several features in common. It is the purpose of the present paper to present a consistent theory of the transpiration method.

As the flow rate of carrier gas, $\dot{n}_1$, is varied, three regions of interest can be described. They are: *1.* very small $\dot{n}_1$, a considerable amount of sample vapour is transported by a diffusion mechanism as well as by bulk hydrodynamic flow, *2.* moderate $\dot{n}_1$, most vapour transport is dependent on bulk hydrodynamic flow, and *3.* large $\dot{n}_1$, the gas in the sample compartment is not saturated with sample vapour.

The case in which the flow of carrier gas is so rapid that it is no longer saturated in the sample compartment, region *3* above, has been considered in detail by Hofmeister, Haeseler, and Glemser.[5] Merten and Bell[3] have discussed the kinetic aspects of the transpiration method, and found that at high flow rates, saturation of the carrier gas may be prevented by incomplete mixing in the gas stream or by insufficiently rapid vaporization of the sample. For the latter case these authors considered the application of the Langmuir equation, including a vaporization coefficient, for values of the rate of vaporization of the condensed sample. This case will not be considered further in this paper.

The flow of sample vapour in regions *1* and *2* can be considered together in the treatment to be presented since, in addition to bulk hydrodynamic flow, diffusive flow always occurs. This diffusion increases the total mass transport from the condensed sample, and is consequently of importance for the vapour pressure determination.

Several attempts have been made to give a quantitative description of the diffusion effects in the transpiration method.[3,5-8] In the present paper we will discuss the theory of this method, based on the proper definitions of diffusion and laminar viscous flow. Furthermore, diffusion in both the "upstream" and "downstream" directions will be considered.

THEORY

Case 1. Flow of vapour through exit capillary. We have discussed elsewhere[4] the equations for coupled diffusion and viscous flow. The appropriate equation for a binary system is

$$J_i = -Dc(dx_i/dz) + cx_i v \qquad (1)$$

where J_i is the flux of species i in mol s^{-1} cm^{-2} in the z direction, x_i is the mol fraction of species i, c is the total gas concentration in mol cm^{-3}, v is the mean molecular velocity in the z direction, and D is the gaseous diffusivity coefficient.[4,9,10]

Let subscripts 1 and 2 represent the two gaseous species in the transpiration experiment, carrier gas and sample vapour, respectively.

Experimentally one considers the case of a uniform temperature and a uniform flow rate of carrier gas. One wishes to interrelate the flux of sample vapour, J_2, to the equilibrium vapour pressure of the sample.

One may solve the differential equation (1) and obtain as a solution

$$x_{2z} = (J_2/cv)[1 - \exp{(cvz/Dc)}] + x_{2i} \exp{(cvz/Dc)} \qquad (2)$$

where x_{2z} is the value of the mol fraction of the vapour at $z=z$ and x_{2i} is the value at $z=0$. Consider the case of $z=l$, and assume that the sample vapour is dissipated completely at the end of the capillary. This assumption may be represented by $x_{2l}=0$. For this case, rearrangement of eqn. (2) gives

$$J_2 = x_{2i}cv/[1 - \exp{(-cvl/Dc)}] \qquad (3)$$

In our subsequent paper,[4] we show that v is the sum of two velocities; i.e., v_d and v_v, where v_d is a velocity caused by diffusion and v_v is a velocity caused by a pressure gradient. These velocities are

$$v_d = \frac{D(1-\gamma)}{\gamma + x_1(1-\gamma)} (dx_1/dz) \qquad (4)$$

and

$$v_v = (-r^2/8\eta)(dP/dz) \qquad (5)$$

where $\gamma = \sqrt{M_2/M_1}$, M_i is the molecular weight, P is the pressure, r is the capillary radius and η is the viscosity. Replacing v in the numerator of eqn. (3) with eqns. (4) and (5), one has

$$J_2 = \frac{x_{2i}c\left(\dfrac{D(1-\gamma)}{\gamma + x_1(1-\gamma)} (dx_1/dz) - (r^2/8\eta)(dP/dz)\right)}{1 - \exp{(-cvl/Dc)}} \qquad (6)$$

Eqn. (6) may be rearranged and integrated over z, x_1 and P with values valid from the capillary entrance to the capillary exit. Assume that both gases are ideal, and that D and η are independent of z. With Dalton's law applied to the sample compartment, the ratio of the sample equilibrium vapour pressure to the total pressure is $P_{si}/P_i = x_{si}$, and one obtains

$$P_{si}{}^2 = x_{si}{}^2 P_f{}^2 + (16\eta R T x_{si} l/r^2)\{J_s[1 - \exp\,(-(J_1 + J_s)l/Dc)] + (x_{si}D'/lRT)\,\ln\,[1 - x_{si}(1 - \gamma)]\} \quad (7)$$

where P_f is the pressure at the exit of the capillary and D' is DP. Replacing cv in the numerator of eqn. (3) by the equation

$$J_1 + J_s = cv \quad (8)$$

which may be derived from eqn. (1) by use of the simple properties of the mol fraction, one has

$$x_{si} = (J_s/(J_1 + J_s))[1 - \exp\,(-cvl/Dc)] \quad (9)$$

We identify terms assumed to be constant in eqns. (7) and (9) by

$$A = \pi r^2 D'/RTl \quad (10)$$

and

$$C = \pi r^4/(16RTl\eta) \quad (11)$$

Introducing also the equation

$$J_i = \dot{n}_i/(\pi r^2) \quad (12)$$

where $\dot{n}_i$ is the flow rate of species i in mol s^{-1}, we may rewrite eqns. (7) and (9) as

$$P_{si}{}^2 = x_{si}{}^2\{P_f{}^2 + (\dot{n}_1 + \dot{n}_s)/C + (A/C)\,\ln\,[1 - x_{si}(1 - \gamma)]\} \quad (13)$$

and

$$x_{si} = [\dot{n}_s/(\dot{n}_1 + \dot{n}_s)][1 - \exp\,(-(\dot{n}_1 + \dot{n}_s)/A)] \quad (14)$$

Eqns. (13) and (14) give a relationship valid for the calculation of the sample equilibrium vapour pressure, P_{si}, at temperature T as determined by the two flow rates $\dot{n}_1$ and $\dot{n}_s$. These equations consider flow of materials only through the exit capillary of the apparatus. A direct application could be made to the experimental case in which the sample vapour transport, $\dot{n}_s$, is determined from the condensate in the "downstream" cold region of the apparatus. In this case the only measured values of $\dot{n}_s$ are for flow in the exit capillary.

It is of interest to discuss the value of $\dot{n}_s$ when the flow of carrier gas goes to zero, $\dot{n}_1 = 0$. In this case from eqns. (13) and (14) one has

$$P_{si}{}^2 = x_{si}{}^2\{P_f{}^2 + \dot{n}_s/C + (A/C)\,\ln\,[1 - x_{si}(1 - \gamma)]\} \quad (13z)$$

and

$$x_{si} = 1 - \exp\,(-\dot{n}_s/A) \quad (14z)$$

These equations are exactly the same as those derived by us in a subsequent paper,[4] in which we consider the experimental case of $\dot{n}_1 = 0$.

Case 2. Flow of sample vapour through both entrance and exit capillaries. In addition to the flow and diffusion of carrier gas and sample vapour in the exit capillary, sample vapour may diffuse "upstream" through the entrance capillary. This effect may be important in experimental cases in which the sample vapour transport, $\dot{n}_s$, is determined by measuring the mass loss of the sample.

For the entrance capillary we consider the z' coordinate as shown in Fig. 1. It is to be noted that when sample vapour leaves the apparatus through the entrance capillary with this choice of z' coordinate, $\dot{n}_s > 0$, whereas $\dot{n}_1 < 0$ because the carrier gas is flowing toward negative z'. For the entrance capillary, equations (13) and (14) should be applicable with the replacement of $\dot{n}_1$ by $-\dot{n}_1$. Thus,

$$P_{si}{}^2 = x_{si}{}^2\{P_{fe}{}^2 + (\dot{n}_{se} - \dot{n}_1)/C_e + (A_e/C_e)\,\ln\,[1 - x_{si}(1 - \gamma)]\} \quad (13e)$$

and

$$x_{si} = [\dot{n}_{se}/(\dot{n}_{se} - \dot{n}_1)][1 - \exp\,(-(\dot{n}_{se} - \dot{n}_1)/A_e)] \quad (14e)$$

A subscript e has been added to quantities which will be different for the entrance capillary from those of the exit capillary. The quantities x_{si} and P_{si} are the same for both sets of equations since these quantities apply to the sample compartment. It is assumed that the gas in the sample compartment is of uniform composition and pressure.

By equating (14) and (14e) one obtains a relationship between $\dot{n}_s$ and $\dot{n}_{se}$, and one is able to calculate the amount of sample vapour transported by diffusion through the entrance capillary.

Two cases are of interest:

Case A. $\dot{n}_1 = 0$. This gives

$$\dot{n}_{2c}/A_c = \dot{n}_2/A \qquad (15)$$

With equal capillary dimensions, $A_c = A$ and $\dot{n}_{2c} = \dot{n}_2$.

Case B. $\dot{n}_1 \gg 0$, $\dot{n}_2$, $\dot{n}_{2c}$. In this case one has

$$-(\dot{n}_{2c}/\dot{n}_1)[1-\exp(\dot{n}_1/A_c)] =$$
$$(\dot{n}_2/\dot{n}_1)[1-\exp(-\dot{n}_1/A)] \qquad (16)$$

and if $\dot{n}_1 \gg A$, then

$$\dot{n}_{2c} = \dot{n}_2 \exp(-\dot{n}_1/A_c) \qquad (17)$$

Clearly the equation resulting from the addition of (13) to (13e) is very complex, and its application is not practical since it contains too many unknown parameters.

DISCUSSION

Reduction to Merten's theory. Merten[8] has presented a theoretical approach to the transpiration experiment. He assumed that the pressure is uniform throughout the transpiration apparatus. One may obtain Merten's equation from equations (13) and (14) by assuming that $C = \infty$ and that $\dot{n}_1 \gg \dot{n}_2$. The assumption that $C = \infty$ is equivalent to assuming that $\eta = 0$; *i.e.*, the gas has no viscosity. With no viscosity there would be no resistance to flow of gas, and no pressure gradient would result. From the assumption that $\dot{n}_1 \gg \dot{n}_2$, one neglects $\dot{n}_2$ in terms in which the sum of $\dot{n}_1$ and $\dot{n}_2$ appears. Thus, equations (13) and (14) reduce to

$$\dot{n}_2 = \dot{n}_1 \frac{P_{2i}}{P_f} \left[1 - \exp(-\dot{n}_1/A) \right]^{-1} \qquad (18)$$

which is Merten's equation.

The main advantage of the present theoretical development is that no assumption regarding uniform pressure is made. In most experiments pressure gradients are not evaluated, and it would be extremely difficult to make the necessary measurements. In order to have large flow rates of carrier gas, a pressure gradient is required. The assumption of no pressure gradient appears to be somewhat unrealistic.

Comparison of results of theories. In Fig. 2 are given calculated curves of the vapour flow rate $\dot{n}_2$ vs. carrier gas flow rate $\dot{n}_1$ which were generated by the equations for the following cases: *1*, the present theoretical development
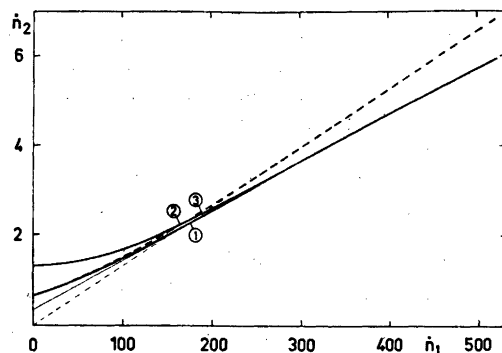

Fig. 2. Calculated curves of vapour flow rate $\dot{n}_2$ vs. carrier gas flow rate $\dot{n}_1$ in a transpiration experiment.
1. Present theory, diffusion through exit capillary only.
2. Present theory, diffusion through both entrance and exit capillaries.
3. Merten's[8] theory, diffusion through exit capillary only, and assuming no pressure drop in the apparatus.

considering only vapour flow from the exit capillary, eqns. (13) and (14); *2*, the results given in case *1* above with the addition of sample vapour transport through the carrier gas entrance capillary, assuming the same A value for both capillaries and *3*, the results given by Merten's eqn. (18) assuming that there is no pressure drop in the apparatus. The same values for P_{2i}, P_f and A were used for all three curves.

In comparing the resulting curves of cases *1* and *3*, one notes that the curves are identical at small flow rates of carrier gas, $\dot{n}_1$ small. This is a reasonable result since the effect of viscous flow caused by a pressure gradient should be small when $\dot{n}_1$ is small.

At large flow rates of carrier gas, $\dot{n}_1$ large, the neglect of the viscosity of the vapour causes a difference between the two curves. It is reasonable that the difference between the two curves increases with increasing $\dot{n}_1$ since a larger pressure gradient is needed to cause the flow, and the effect of viscous flow will increase.

At larger flow rates of carrier gas, one may neglect the effect of vapour transport by diffusion. In the equations this may be done by setting $A = 0$. Eqn. (13) then reduces to

$$\dot{n}_2 = \dot{n}_1 \frac{P_{2i}}{\left(P_f^2 + \frac{\dot{n}_1 + \dot{n}_2}{C}\right)^{\frac{1}{2}} - P_{2i}} \qquad (19)$$

and Merten's equation, eqn. (18), reduces to

$$\dot{n}_2 = \dot{n}_1 \frac{P_{2i}}{P_f} \qquad (20)$$

With fixed values of P_f, P_{2i} and C, one may see that the dependence of $\dot{n}_2$ on $\dot{n}_1$ in our theory is non-linear, whereas there is a linear dependence in Merten's theory.

Thus, with the present theoretical development, data in the large $\dot{n}_1$ range are not linear. A straight line through this apparently linear range will have a non-zero intercept. This is contrasted with an actual zero intercept in Merten's theory.

Merten's assumption that $C = \infty$ gives a too low value for P_{2i}, while his assumption that $\dot{n}_1 \gg \dot{n}_2$ causes a too high value. In most practical cases the former effect is the larger. From the calculated curve 1 in Fig. 2 the difference between the pressure values from the two theories is about 10 %. Since C is proportional to r^4 [eqn. (11)], a smaller capillary radius will favour our theory.

We are presently performing measurements to determine experimentally the significance of our theory in relation to that of Merten.

The effect of diffusion. Diffusion of vapour through the entrance capillary in opposition to the flow direction of the carrier gas has been mentioned by Merten and Bell.[3] In the present paper the first attempt has been made to evaluate the contribution of the back diffusion.

In viewing curves *1* and *2* in Fig. 2, one notes that the gaseous diffusion through the entrance capillary does make a significant contribution to the vapour flow rate at small values of $\dot{n}_1$. For $\dot{n}_1 = 0$, the transport of sample vapour is increased with a factor of 2, when the capillary dimensions are equal.

At large flow rates of carrier gas, however, the diffusion contribution becomes very small. In both Merten's[3] and the present theoretical development terms of the type $[1 - \exp(-\dot{n}_1/A)]$ or $[1 - \exp(-(\dot{n}_1 + \dot{n}_2)/A)]$ are related to the diffusion transport mechanism. Thus, when the exponential expression is small compared to unity, diffusion may be neglected, *e.g.*, diffusion contributes less than 5 % to the

transport of sample vapour when $\dot{n}_1/A > 3$.

From this discussion the nearly linear range of carrier gas flow rates for which the diffusion contribution is small, is determined by the parameter A. According to eqn. (10), A is dependent on r, l, T, and D'. From the kinetic theory of gases it is expected that D' is proportional to $T^{3/2}$, but is independent of pressure. Thus, the parameter A should be dependent on $r^2 T^{\frac{1}{2}}/l$, and the nearly linear range of carrier gas flow rates should depend on the capillary dimensions and the square root of temperature. This means that the equilibrium vapour pressure of the sample is of little importance for the determination of this range.

Recommendations for users of the transpiration method. In using the transpiration method for determining equilibrium vapour pressures, one should do the following.

1. One should determine experimentally a curve of the type shown in Fig. 2. This requires experimental determinations of $\dot{n}_2$ at varying $\dot{n}_1$ with fixed temperature T and hence fixed P_{2i}. This curve will delineate the nearly linear range, which is desired for laboratory measurements, from the diffusion range at small $\dot{n}_1$ and from the desaturation range at large $\dot{n}_1$. (In principle, by avoiding the desaturation range, the equilibrium vapour pressure P_{2i} and the parameters A and C could be determined from any set of $\dot{n}_1$, $\dot{n}_2$ and P_f data by fitting eqns. (13) and (14) to the data.)

2. From the data acquired above for the nearly linear range (small diffusion and no desaturation), determine the values of P_{2i} and C by a non-linear least squares computer program using eqn. (19).

3. Restrict measurements for vapour pressure determinations to $\dot{n}_1$ values in the nearly linear range. Rearranging eqn. (19), one has

$$P_{2i} = \frac{\dot{n}_2}{\dot{n}_1 + \dot{n}_2}\left(P_f^2 + \frac{\dot{n}_1 + \dot{n}_2}{C}\right)^{\frac{1}{2}} \qquad (21)$$

Use eqn. (21) to calculate the equilibrium vapour pressure at other temperatures.

In case the vapour pressure is known, the data can be used to determine the molecular weight of the vapour. One may use the equation

$$\dot{n}_2 = \dot{m}_2/M_2 \qquad (22)$$

where $\dot{m}_2$ is the measured mass of vapour carried away from the sample per unit time, and M_2 is the molecular weight of the vapour. By inserting eqn. (22) into eqn. (21), one may use the same procedure as described above to determine the molecular weight of the vapour.

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