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A Thermogravimetric Method for Determination of Vapour Pressures Above 10^{-2} Atm. I: Theory

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Available methods for the determination of vapour pressures at high temperatures appear to leave a demand for an experimentally simple method for the measurement of pressures above the range of molecular flow. A method originating from the early work of Ruff and co-workers is considered for the purpose. In this method, the rate of vapour transport through a capillary is determined as a function of an applied inert-gas pressure at constant furnace temperature. The theory of the method is developed, based on transport equations for a binary gas mixture with gradients in both composition and total pressure. Effects of interdiffusion, viscous flow and thermal transport are considered, and the ranges for dominating influence of each of these effects are delineated. It is shown how computer fitting of the theoretical equation to the experimental data advantageously may be used to determine the equilibrium vapour pressure. Applications to the determination of vapour diffusivity and viscosity also are considered.

The study of vaporization processes forms an important part of high-temperature chemical research. In the present context, vaporization is taken to include all processes whereby gas is evolved from a system of condensed phases, and vapour pressure determinations include the measurement of equilibrium gas pressures in any such system.

For the study of high-temperature systems, the effusion method has been used extensively. The effusion method, however, is based on molecular flow and hence is limited to pressures below *ca.* 10^{-4} atm. The present paper discusses a method for the higher pressure range (about 10^{-2} to 1 atm), equally applicable at elevated temperatures because the vapour pressure cell employed is comparable to an effusion cell in simplicity.

The chosen method originates from the early work of Ruff *et al.*[1,2] The substance or system to be investigated is contained in a cell with a narrow capillary opening in the lid. The cell is suspended from a balance into a furnace in an inert-gas atmosphere which initially is at a higher pressure than the equilibrium vapour pressure of the system at the furnace temperature. When the inert-gas pressure is lowered (or the vapour pressure is increased by increasing the temperature), the vapour transport through the opening and hence the rate of mass loss from the cell increase. The enhanced flux particularly is marked when the inert-gas pressure becomes smaller than the equilibrium vapour pressure, and this effect may be used to determine the vapour pressure.

Ruff *et al.*[1,2] and J. Fischer[3] followed the mass change of the cell at constant inert-gas pressure and increasing temperature. From their measurements it was found that a graph of the mass *versus* time or temperature did not exhibit a sharp break at the equilibrium vapour pressure. The situation was not improved substantially by plotting instead the derivative of mass with respect to time (*i.e.*, the rate of mass loss). W. Fischer *et al.*[4] pointed out the advantages of observing mass changes at constant temperature and decreasing pressure stepwise. However, a really sharp break in the

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curve for rate of mass loss *versus* pressure was not found.

A subsequent theoretical treatment by Wagner[5] showed that the mentioned curves cannot be expected to give sharp breaks. Wagner gave recommendations as to the best way of performing the experiments, but even so the graphical method for determination of the equilibrium pressure remains unreliable.

It is the purpose of the present paper (1) to develop a consistent theory for the method, (2) to discuss the resulting equation in terms of various assumptions that lead to simpler equations as limiting cases, and (3) to show how a numerical rather than graphical procedure may be used to determine the equilibrium vapour pressure from the experimental observations.

THEORY

A schematic drawing of a suitable cell is shown in Fig. 1. The opening has the shape of a capillary with radius r and length l. The cell is suspended inside a furnace at temperature T. The inert gas is denoted by subscript 1 and the vapour by subscript 2, while subscript f denotes the furnace space and subscript i denotes the interior of the cell. The symbol c denotes concentration, x mol fraction, and P pressure.

The following assumptions are made:

(1) The system is maintained at a steady state, with a net transport $\dot{n}_2$ (mol/s) of vapour through the capillary, while the net transport of inert gas, $\dot{n}_1 = 0$. The flux $J_2 = \dot{n}_2/(\pi r^2)$.

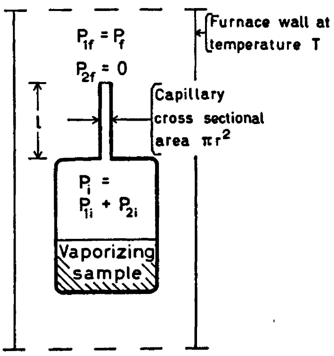

Fig. 1. Schematic diagram of the cell suspended inside the furnace.

(2) At the exit end of the capillary, the vapour dissipates quickly to colder parts of the furnace because of diffusion and convection, so that $x_{1f} = 1$, $x_{2f} = 0$ and $P_{1f} = P_f$, $P_{2f} = 0$.

(3) The capillary is narrow in order to suppress the diffusive flux, and a significant pressure drop may exist through the capillary ($P_i > P_f$). The rate of mass transport is dependent on the rate of viscous flow caused by this pressure drop.

(4) The steady-state evaporation will cause the temperature of the sample to be lower than the observed furnace temperature T, which means that the vapour pressure P_{2i} inside the cell may be lower than the equilibrium vapour pressure $P_2°$ at the temperature T.

As regards assumption (3), Wagner[5] assumed instead that the pressure remains uniform through the capillary. This assumption limits the applicability of his result to certain experimental conditions, which is the reason why a new treatment appeared to be necessary.

Transport equations for simultaneous diffusion and flow

The first task is to find the correct transport equations for the case of a binary mixture of ideal gases with simultaneous gradients in composition and total pressure. This is a case which appears to have received only occasional attention in the literature. Texts on interdiffusion of gases quite commonly state Fick's first law in terms of gradients in concentration:

$$J_{1d} = -D_{12}(\mathrm{d}c_1/\mathrm{d}z) \qquad \text{(a)*}$$

$$J_{2d} = -D_{21}(\mathrm{d}c_2/\mathrm{d}z) \qquad \text{(b)}$$

where D_{12} and D_{21} are the coefficients of interdiffusion for the two gases, and z is the direction of the capillary axis.

An objection to these equations may be raised. Let us introduce the mol fractions $x_1 = c_1/c$, $x_2 = c_2/c$. Rewriting eqn. (a) gives:

$$J_{1d} = -D_{12}\frac{\mathrm{d}(cx_1)}{\mathrm{d}z} = -D_{12}\left(c\frac{\mathrm{d}x_1}{\mathrm{d}z} + x_1\frac{\mathrm{d}c}{\mathrm{d}z}\right) = -\frac{D_{12}}{RT}\left(P\frac{\mathrm{d}x_1}{\mathrm{d}z} + x_1\frac{\mathrm{d}P}{\mathrm{d}z}\right) \qquad \text{(c)}$$

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* Letters are used here to identify equations which should not be accepted without reservations.

According to Chapman and Cowling[6] diffusion should be considered as a process caused by a gradient in composition, while flow is a process caused by a gradient in total pressure. It is then apparent that the second term to the right in eqn. (c) does not belong in the expression for the diffusive flux, and therefore eqns. (a) and (b) are not appropriate. The diffusive flux should be expressed in terms of the derivative of the mol fraction.

The total fluxes J_1 and J_2 for the case of gradients in both composition and total pressure may be expressed by the general equations[7,8]

$$J_1 = -D_{12}c\frac{\mathrm{d}x_1}{\mathrm{d}z} + cx_1v \tag{1}$$

$$J_2 = -D_{21}c\frac{\mathrm{d}x_2}{\mathrm{d}z} + cx_2v \tag{2}$$

In these equations, v is the mean molecular velocity in the z direction. In order to derive the correct expression for the velocity v, we will consider first the equations for the special case that the total pressure is uniform.

The case of uniform pressure. The original experimental work of Graham showed that the diffusive fluxes are inversely proportional to the square root of the molecular masses, a result that also may be deduced from a consideration of momentum transfer.[9] Thus, at uniform pressure $J_{2\mathrm{d}} \neq J_{1\mathrm{d}}$. The transport equations for this case may be formulated in two ways. One may use equations analogous to eqns. (1) and (2) with $v=0$, using the symbols D_1 and D_2 for the diffusivities to emphasize that they are not equal:

$$J_{1\mathrm{d}} = -D_1c(\mathrm{d}x_1/\mathrm{d}z) \tag{3}$$

$$J_{2\mathrm{d}} = -D_2c(\mathrm{d}x_2/\mathrm{d}z) \tag{4}$$

The diffusivities are related through Graham's law of diffusion:

$$-\frac{J_{1\mathrm{d}}}{J_{2\mathrm{d}}} = \frac{D_1}{D_2} = \sqrt{\frac{m_2}{m_1}} = \gamma \tag{5}$$

in which m_1 and m_2 are the molecular masses, and the symbol γ has been introduced for brevity of notation.

On the other hand, one may preserve the concept of equal interdiffusion coefficients, that is, $D_{12} = D_{21} = D$. In this case the net transport may be expressed in terms of a mean molecular velocity in the z direction, designated v_d to indicate that this mean velocity arises from the process of diffusion alone, in the absence of a pressure gradient. Thus, one has

$$J_{1\mathrm{d}} = -Dc\frac{\mathrm{d}x_1}{\mathrm{d}z} + cx_1v_\mathrm{d} \tag{6}$$

$$J_{2\mathrm{d}} = -Dc\frac{\mathrm{d}x_2}{\mathrm{d}z} + cx_2v_\mathrm{d} \tag{7}$$

The velocity v_d may be calculated by equating the fluxes from eqns. (3) and (6), and from eqns. (4) and (7), introducing also $\mathrm{d}x_2/\mathrm{d}z = -\mathrm{d}x_1/\mathrm{d}z$, and substituting eqn. (5). This gives

$$v_\mathrm{d} = \frac{D(1-\gamma)}{\gamma + x_1(1-\gamma)}\,\frac{\mathrm{d}x_1}{\mathrm{d}z} \tag{8}$$

Introduction of eqn. (8) in eqns. (6) and (7) yields the expressions for the diffusive fluxes at uniform total pressure.

The case of gradients in both composition and total pressure. A gradient in pressure causes a viscous flow (assuming moderate pressure gradients so that turbulence does not occur). The viscous flow may be described in terms of its mean linear velocity v_visc. For a straight, cylindrical tube with radius r, this velocity is given by

$$v_\mathrm{visc} = -\frac{r^2}{8\eta} \times \frac{\mathrm{d}P}{\mathrm{d}z} \tag{9}$$

where η is the viscosity of the gas mixture.

The fluxes caused by diffusion and by viscous flow are additive.[9] This may be expressed by the equations $J_1 = J_{1\mathrm{d}} + J_{1\mathrm{visc}}$; $J_2 = J_{2\mathrm{d}} + J_{2\mathrm{visc}}$, or by the equivalent statement that the velocity in eqns. (1) and (2) is the sum of two separate contributions:

$$v = v_\mathrm{d} + v_\mathrm{visc} \tag{10}$$

Substitution of eqn. (10) into eqns. (1) and (2), with v_d given from eqn. (8) and v_visc given from eqn. (9), yields the expressions for the fluxes caused by gradients in both composition and total pressure. These equations need not be written for the present purpose.

Application to the vapour pressure method

In the experimental arrangement shown in Fig. 1 at steady state, the net flux is equal to the mean molecular velocity multiplied by the total concentration. That is,

$$J_2 = cv \tag{11}$$

With $J_1 = 0$ in eqn. (1) we also have

$$cv = cD\frac{\mathrm{d}\ln x_1}{\mathrm{d}z} \tag{12}$$

From the kinetic theory of gases it is known that the gas diffusivity is inversely proportional to the total pressure, that is

$$DP = D' \tag{13}$$

where D' is a constant at constant temperature.

With substitution of c and J_2, eqns. (11), (12) and (13) give

$$\mathrm{d}\ln x_1 = \frac{RT\dot{n}_2}{\pi r^2 D'}\mathrm{d}z \tag{14}$$

Integration between $z=0$ and $z=l$ yields after some rearrangement:

$$x_{1\mathrm{i}} = \exp(-\dot{n}_2/A) \tag{15}$$

The parameter A, which is constant for a given experiment at constant temperature, is defined by

$$A = \frac{\pi r^2 D'}{RTl} \tag{16}$$

The total pressure P_i inside the cell may be expressed in terms of the partial pressures, and we have

$$P_\mathrm{i} = \frac{P_{2\mathrm{i}}}{1-\exp(-\dot{n}_2/A)} \tag{17}$$

We now turn to eqn. (11) again. Introduction of eqns. (8), (9) and (10) yields

$$\dot{n}_2\,\mathrm{d}z = -\frac{\pi r^4}{8RT\eta}P\,\mathrm{d}P + \frac{\pi r^2 D'}{RT} \times$$

$$\frac{1-\gamma}{\gamma+(1-\gamma)x_1}\mathrm{d}x_1 \tag{18}$$

According to the kinetic theory, the viscosity of a gas is independent of pressure, while it is expected to vary with the gas composition. For the latter reason, the value of the viscosity would be expected to vary along the capillary, but we will approximate by the assumption that η is a constant. Eqn. (18) then may be integrated between $z=0$ and $z=l$, *i.e.*, between $x_1 = x_{1\mathrm{i}}$, as given by eqn. (15), and $x_1 = 1$. This gives

$$\dot{n}_2 = \frac{\pi r^4}{16RTl\eta}\left(P_\mathrm{i}^2 - P_\mathrm{f}^2\right) -$$

$$A\ln\left[\gamma+(1-\gamma)\exp(-\dot{n}_2/A)\right] \tag{19}$$

For brevity we define another parameter, constant for a given experiment at constant temperature:

$$C = \frac{\pi r^4}{16RTl\eta} \tag{20}$$

Eqns. (17) and (20) introduced in eqn. (19) give

$$\dot{n}_2 = C\left[\left(\frac{P_{2\mathrm{i}}}{1-\exp(-\dot{n}_2/A)}\right)^2 - P_\mathrm{f}^2\right] -$$

$$A\ln\left[\gamma+(1-\gamma)\exp(-\dot{n}_2/A)\right] \tag{21}$$

The effect of sample cooling

The evaporation requires heat, and the necessary heat flux requires that the sample temperature T_s is slightly lower than the constant furnace temperature T (*cf.* assumption (4) in the introduction). This effect was considered by Wagner.[5] Assuming a heat transfer coefficient K specific to the given experimental arrangement, one has

$$K(T-T_\mathrm{s}) = \dot{n}_2\Delta H_\mathrm{v}$$

where ΔH_v is the molar heat of vaporization of the sample.

The lowered sample temperature causes a lowered vapour pressure in accordance with the Clausius-Clapeyron equation:

$$\ln\frac{P_{2\mathrm{i}}}{P_2^\circ} = \frac{\Delta H_\mathrm{v}}{R}\left(\frac{1}{T}-\frac{1}{T_\mathrm{s}}\right) \cong -\frac{\Delta H_\mathrm{v}}{RT^2}(T-T_\mathrm{s})$$

Combination of these two equations yields

$$P_{2\mathrm{i}} = P_2^\circ\exp(-\dot{n}_2/B) \tag{22}$$

where the parameter B, a constant for a given experiment at constant temperature, is given by the expression

$$B = KRT^2/\Delta H_\mathrm{v}^2 \tag{23}$$

Introducing eqn. (22) in eqn. (21) we get the complete equation for the rate of mass transport:

$$\dot{n}_2 = C\left[\left(\frac{P_2^\circ\exp(-\dot{n}_2/B)}{1-\exp(-\dot{n}_2/A)}\right)^2 - P_\mathrm{f}^2\right] -$$

$$A\ln\left[\gamma+(1-\gamma)\exp(-\dot{n}_2/A)\right] \tag{24}$$

in which the parameter γ is given by eqn. (5), A by eqn. (16), C by eqn. (20), and B by eqn. (23).

DISCUSSION

An experiment using a thermobalance yields a record of the mass of the cell with sample as a function of time. From the slope of the recorded curve, the rate of mass loss is determined. The inert-gas pressure in the furnace is read on a manometer, and is lowered stepwise in the course of the experiment. Thus, one obtains a set of corresponding values for $\dot{n}_2$ and P_f, which may be considered as the "knowns" in eqn. (24). For the present we will consider also the parameter $\gamma = (M_2/M_1)^{\frac{1}{2}}$ as known, where M_1 and M_2 are the molecular weights of the inert gas and of the vapour. In a later section we will return to the question of unknown molecular weight of the vapour.

The parameters A, B and C are generally unknown, as is also the vapour pressure P_2°. Thus, there are four unknowns to be determined. The problem may be handled by means of a suitable, non-linear least-squares analysis computer program which fits eqn. (24) to the observed set of data. In this way one obtains the "best" values for the parameters A, B and C, and for P_2°. There is in principle no objection to this procedure. It may happen, however, that eqn. (24) may be fitted to a given set of experimental data with almost equal precision for widely different sets of values for the two parameters B and C. This feature of the equation will be made clear in the discussion to follow. Hence, it is of interest to consider simplifications of eqn. (24) by removal of either B or C.

The course of an experiment roughly may be divided in two parts. At the outset, $P_f > P_2^\circ$, and the mass transport occurs mainly by diffusion of vapour through a higher pressure of inert gas. The rate of mass loss is low and is determined primarily by the value of the parameter A.

In the later stage of the experiment, $P_f < P_2^\circ$, and the rate of mass loss is high. It is determined mainly either by the resistance to viscous flow through the capillary, or by the rate of heat transfer to the sample, or by a combination of both effects. These two effects are connected with the values of the parameters C and B, respectively. Each of the two limiting cases will be discussed separately.

First case: Viscous flow is rate determining

In this case it is assumed that the sample temperature remains closely equal to the furnace temperature T, so that the vapour pressure inside the cell effectively is maintained at the value P_2° throughout the experiment. Formally this corresponds to an infinite heat transfer coefficient K in eqn. (23). This means an infinite value of B, which makes the exponential in the numerator of eqn. (24) go to unity (that is, eqn. (21) is recovered, with $P_{2i} = P_2^\circ$).

For the purpose of the present discussion it is convenient to express the equation in terms of the ratio P_f/P_2°, which for brevity is denoted by y:

$$\dot{n}_2 = C(P_2^\circ)^2\left[\left(\frac{1}{1-\exp(-\dot{n}_2/A)}\right)^2 - y^2\right] - A\ln\left[\gamma + (1-\gamma)\exp(-\dot{n}_2/A)\right] \qquad (25)$$

The behaviour of this equation will be illustrated by graphs of $\dot{n}_2$ as a function of y. For this purpose a set of arbitrary but reasonable values is chosen for the physical quantities as shown in Table 1, which also gives the corresponding values of the parameters A, C, and γ. The chosen value of M_1 is equal to the atomic weight of argon, while M_2 corresponds roughly to the atomic weight of a metal in the second long period, and the value of the viscosity appears reasonable for a monoatomic metal vapour at the elevated temperature T.

Table 1. Values of constants used for the calculated curves in Fig. 2.

Physical quantities, values chosen	Parameters of eqn. (25), calculated from the chosen physical quantities
$r = 3\times10^{-4}$ m	
$l = 1\times10^{-2}$ m	$A = 5\times10^{-2}\,\mu$mol s^{-1}
$T = 2000$ K	
$D' = D\times P = 30$ N s^{-1}	$C = 5\times10^{-8}\,\mu$mol s^{-1} Pa^{-2}
$\eta = 1.1\times10^{-4}$ N s m^{-2}	
$M_1 = 40$	$\gamma = 1.58$
$M_2 = 100$	

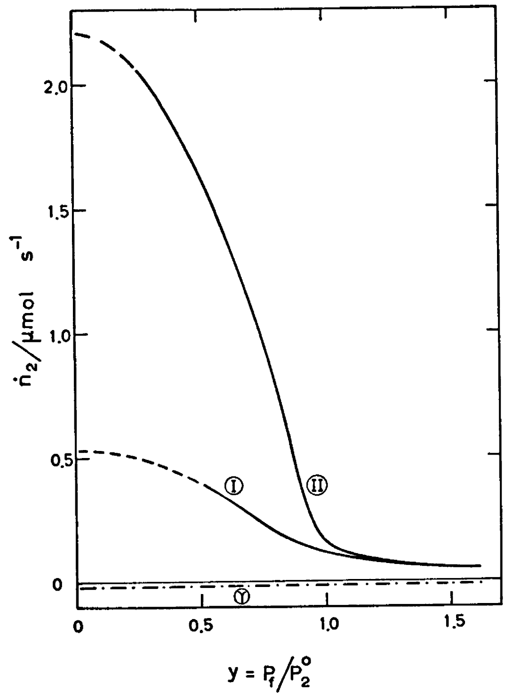

Fig. 2. Curves for the rate of mass loss $\dot{n}_2$ as a function of y, calculated from eqn. (25) with the parameters given in Table 1. Curve I: $P_2^\circ = 3333$ Pa ($= 25$ Torr); Curve II: $P_2^\circ = 6666$ Pa ($= 50$ Torr); Curve γ: Second term of eqn. (25) plotted separately (closely identical for both vapour pressure values).

Values of $\dot{n}_2$ have been calculated with these parameter values for two different vapour pressures, and the results are shown as curves I and II in Fig. 2. In addition, the second term of eqn. (25), the "γ term", is plotted separately (bottom curve).

Several features of the graph, Fig. 2, should be noted. First, it is seen that the "γ term" tends toward a small, constant value for $y < 1$, and that this term makes only a minor contribution (in this case, a negative contribution) to the calculated values of $\dot{n}_2$. Omission of this term from the equation would move the calculated curves slightly upwards, with hardly any perceptible change in the shape of the curves. This means that the method may be used also without a knowledge of the molecular weight of the vapour. Preferably, one may estimate the molecular weight of the vapour and include the "γ term" on this basis.

It is noted from Fig. 2 also that the rate of mass loss in the diffusion range ($y > 1$) tends toward the same value for both curves, independent of the vapour pressure, owing to the fact that diffusivity is inversely proportional to pressure. In the viscous flow range ($y < 1$), on the other hand, the rate of mass loss is approximately proportional to the square of the vapour pressure, which accounts for the large difference in the two curves.

The calculated curves in Fig. 2 have been drawn to $y = 0$ (*i.e.*, $P_f = 0$) for the sake of illustration. It should be noted, however, that the theoretical treatment loses validity for P_f less than about 10 Torr, hence the curves are drawn with broken lines below the corresponding y values.

Except for the factor $1/P_2^\circ$ along the abscissa, the curves in Fig. 2 are identical to the curves one would expect to obtain for $\dot{n}_2$ *versus* P_f from an experiment for a system with the chosen parameter values. It is seen that graphical, linear extrapolation would appear unreliable since the theoretical curves do not exhibit any extended range of linearity.

Second case: Heat transfer is rate determining

In this case it is assumed that the mass transport occurs by diffusion, with no (or negligible) pressure drop through the capillary. Formally it corresponds to zero viscosity, which means that the parameter C is infinite [*cf.* eqn. (20)]. It is noted that the first term inside the parenthesis to the left in eqn. (24) is simply P_i^2, and that for no pressure drop, $P_i = P_f$, so that the two terms in the parenthesis are equal. This yields directly the equation for this case:

$$P_f = P_2^\circ \frac{\exp(-\dot{n}_2/B)}{1 - \exp(-\dot{n}_2/A)} \qquad (26)$$

Eqn. (26) does not appear in Wagner's publication.[5] In handling the equations he introduced certain simplifying approximations, and arrived at the equation

$$P_f = P_2^\circ\ (1 + \exp(-\dot{n}_2/A) - \dot{n}_2/B) \qquad (27)$$

A numerical check shows that these two equations give closely identical values of $\dot{n}_2$ for $y = P_f/P_2^\circ < 1$, while the results deviate for

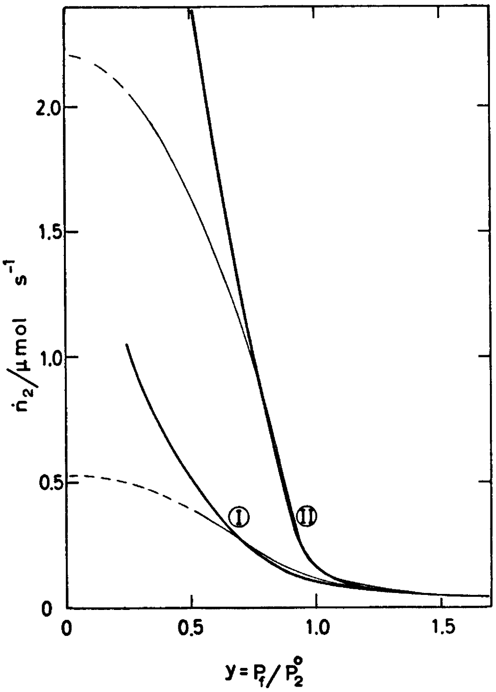

Fig. 3. Comparison of the curves for $\dot{n}_2$ as a function of y, calculated from eqn. (26) (thick lines) and from eqn. (25) (thin lines, identical to those shown in Fig. 2). Curve I: $P_2^\circ = 3333$ Pa, $B = 0.75$ μmol s^{-1}; Curve II: $P_2^\circ = 6666$ Pa, $B = 3.50$ μmol s^{-1}.

$y > 1$. Eqn. (26) may be considered the "corrected Wagner equation" and will be discussed here.

We may investigate to what extent eqn. (26) is able to reproduce the curves calculated from eqn. (25) as shown in Fig. 2. The same value of the parameter A is used. As regards pressures, it is seen that eqn. (26) predicts dependence of $\dot{n}_2$ on the relative pressure y only. Two different values of B thus are needed to match the two curves. It is seen in Fig. 3 that by the use of the values 0.75 and 3.50 μmol s^{-1}, the two curves of Fig. 2 are reproduced by eqn. (26) down to y values of about 0.7.

At lower y values, eqn. (26) predicts a steady increase in $\dot{n}_2$, and in fact predicts that $\dot{n}_2$ goes toward infinity when P_f is reduced to zero. This is clearly impossible, and any real, experimental curve would have to bend toward a finite value of $\dot{n}_2$ due to the restriction imposed by the resistance to viscous flow in the capillary.

On the other hand, for y values down to about 0.7, it appears that both eqns. (25) and (26) may be fitted to a given set of experimental data with almost equal precision. A possible consequence is that computer fitting of the complete eqn. (24) may give trouble, because of the relative importance of the two parameters B and C for a given set of experimental data. It is thus of considerable interest to attempt a delineation of the ranges of temperature *etc.*, in which each of the two simplified equations (25) and (26) may be considered valid.

Ranges of validity for the two limiting cases

For this purpose the two equations may be further simplified for $y < 1$. In eqn. (25) the "y term" will be relatively unimportant in this range and may be omitted (*cf.* Fig. 2). Furthermore, for $y < 1$ we have $\dot{n}_2/A \gg 1$ and thus $\exp(-\dot{n}_2/A) \simeq 0$. With these approximations eqn. (25) reduces to

$$\dot{n}_2 = C(P_2^\circ)^2(1 - y^2) \qquad (28)$$

Similarly, eqn. (26) is reduced to

$$\dot{n}_2 = -B \ln y \qquad (29)$$

A decision between the two models may be reached by comparison of the values of $\dot{n}_2$ predicted by these two equations for the same experimental conditions. By analogy with chemical kinetics, heat transfer and viscous flow in this case may be considered as consecutive processes, and whichever gives the lower value of $\dot{n}_2$ represents the rate-determining step.

In order to reach a clear-cut decision we set the ratio of the two predicted values equal to a factor f:

$$\frac{-B \ln y}{C(P_2^\circ)^2(1 - y^2)} = f \qquad (30)$$

The parameter B is proportional to the heat transfer coefficient K, which may be found by assuming heat transfer by radiation:

$$K(T - T_s) = s\varepsilon\sigma(T^4 - T_s^4) \approx 4s\varepsilon\sigma T^3(T - T_s) \qquad (31)$$

in which ε is the emissivity, T_s is the temperature, s is the area of the cell surface, and σ is the Stefan-Boltzmann radiation constant. One may, somewhat arbitrarily, assume a value of 0.5 for the emissivity (alternatively assuming a somewhat higher emissivity combined with a finite resistance to heat flow through the cell wall and the sample). This gives from eqn. (31):

$$K = 2s\sigma T^3 \tag{32}$$

An expression for the enthalpy of vaporization in eqn. (23) is obtained by noting that the molar entropy of vaporization at the boiling point is approximately the same for different substances (Trouton's rule). This may be applied also to a "boiling point" at, *e.g.*, 50 Torr. Thus we have

$$\Delta H_{\mathrm{v}} = T\Delta S_{\mathrm{v}} \tag{33}$$

Introduction of eqns. (20) and (23) in (30), with the substitutions given by eqns. (32) and (33), yields after some rearrangement

$$\frac{T^4}{r^4} = \frac{\pi \Delta S_{\mathrm{v}}{}^2}{32\,R^2\sigma} \times \frac{(y^2-1)}{\ln y} \times \frac{1}{sl\eta} \times (P_2{}^{\circ})^2 f \tag{34}$$

It is chosen to effect a numerical comparison at a value of $y = 0.80$ (*cf.* Fig. 3). For the entropy of vaporization is assumed $\Delta S_{\mathrm{v}} = 130$ J K^{-1} mol^{-1}. The viscosity of gases varies with molecular mass, collision diameter, and temperature; we can do nothing better than to assume a constant value $\eta = 5 \times 10^{-5}$ N s m^{-2} (roughly corresponding to the viscosity of mercury vapour at 200 – 300 °C). We assume a cylindrical cell of 2 cm outside diameter and 3 cm height, this gives the surface area $s = 2.5 \times 10^{-3}$ m^2. The length of the capillary is assumed $l = 1.0 \times 10^{-2}$ m. With the radiation constant $\sigma = 5.67 \times 10^{-8}$ W m^{-2} K^{-4}, and at a chosen pressure $P_2{}^{\circ} = 6666$ Pa ($= 50$ Torr) eqn. (34) gives

$$T/r = 2.2 \times 10^{-6} f^{1/4}\ \mathrm{K\ m^{-1}} \tag{35}$$

Eqn. (35) indicates a direct proportionality between the capillary radius and the temperature required for the change from heat transfer to viscous flow as the main restraint for the rate of mass transport. It is noted also that the parameters s, l and η enter as fourth root and $P_2{}^{\circ}$ as square root in the expression for T/r, which means that eqn. (34) is fairly insensitive to moderate changes in the values of these parameters.

The factor f was introduced in eqn. (30) with the intention that it may be varied over suitable powers of ten. Choosing a value of the capillary radius $r = 0.3$ mm for illustration, one arrives at the following results:

$f = 0.1$	1	10
$T = 371$ K	660 K	1173 K

These results may be expressed as follows: At temperatures below 100 °C, heat transfer accounts for more than 9/10 of the restraints to mass loss. In the range 100 to 900 °C heat transfer and viscous flow are both of importance in determining the rate of mass loss, the two effects becoming of equal importance at about 400 °C. Above 900 °C viscous flow represents more than 9/10 of the restraints to mass loss.

Thus, the Wagner model of heat transfer, expressed by eqn. (26), will be strictly valid only at temperatures near room temperature. The viscous flow model, expressed by eqn. (25), will be valid at temperatures above 900 °C. These conclusions are reasonable, since the efficiency of the heat transfer increases rapidly with increasing temperature. Viscosity, on the other hand, increases with temperature for any gas or vapour, which means that the resistance to viscous flow will be less at low temperatures.

The above conclusions are believed to be of fairly general validity for samples with medium and high thermal conductivity. In particular a fine-grained and loosely packed solid powdered sample may have very low thermal conductivity, which, however, may be enhanced by compaction of the powder and subdivision of the compact to coarser pieces. Still it appears advisable in such cases to regard the above conclusions critically, and to perform a similar evaluation from eqn. (30) onwards with the use of numerical values proper to the case at hand, if it is desired to assess the relative importance of heat transfer and viscous flow resistance.

ON THE PRACTICAL APPLICATION OF THE METHOD

Our applications of the method to date include determinations of vapour pressures of various molten salt systems at temperatures around 600 to 1200 °C. The relative merits of the two simplified eqns. (25) and (26) have been tested by fitting each of these equations to the same set of experimental data, using a non-linear least-squares analysis computer program.[10] It is generally found that the two equations yield nearly the same values for the vapour pressure. This is also to be expected from the proximity of the calculated curves in Fig. 3, as pointed out above. As a consequence, comparison of vapour pressure values obtained from each of the two limiting equations generally will not give information as to which equation is "valid" for the case in hand. Furthermore, when the experimental data have been obtained in a range where resistance to heat transfer and resistance to viscous flow are simultaneously of importance in determining the rate of mass transport, the values obtained separately from eqns. (26) and (25) for the parameters B and C may have little or no physical significance.

From the considerations above, resistance to heat transfer should be particularly significant in experiments at low temperatures. For this effect to be dominating, temperature would have to be so low as to be of little interest in high-temperature chemistry, but effects in the expected direction have been observed in experiments with volatile molecules such as $NaAlCl_4$, *etc.*, where the size of the molecule contributes to a low viscosity. On the other hand, resistance to viscous flow should dominate in measurements at high temperatures, in particular for monoatomic metal vapours where the small collision diameter gives a relatively high vapour viscosity. This has been confirmed by determinations of the vapour pressure of silver in the temperature range 1580 to 1860 °C; the experimental curves obtained in this case are very similar to those shown in Fig. 2. (The physical data given in Table 1 were in fact chosen with the silver experiments in mind.)

The most accurate results for the vapour pressures in general are obtained by computer fitting of the complete eqn. (24). This is achieved by use of a more sophisticated computer program,[11] which then may yield physically acceptable values for the parameters B and C. The viscosity of the vapour in principle may be determined from the value of C when the exact dimensions of the capillary are known, *cf.* eqn. (20). The viscosity value thus obtained, however, will not be very reliable in the general case, since even the best of computer programs will not be able to assess the truly correct values of B and C when both effects are simultaneously of importance. Likewise the interdiffusion coefficient of the vapour and the inert gas may be determined from the value of the parameter A, but again there are sources of error to be considered. Further discussion of the method, including its application to the determination of viscosities and diffusivities, the effect of large difference in molecular weights, and the influence of porous cell materials, will be presented in subsequent communications in conjunction with experimental data.

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