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THE TRANSPIRATION METHOD

by

Ulrich Merten and Wayne E. Bell

July 7, 1961

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CONTENTS

NOMENCLATURE

Symbol	Definition
α	Thermal diffusion factor
α_e	Evaporation coefficient
λ	Length of capillary (assumed value, 2.0 cm)
ρ	Radius of capillary (assumed value, 0.05 cm)
A	Area of capillary, $\pi\rho^2$
c	Vapor density
d	Length of thermal-gradient region
D	Interdiffusion coefficient of carrier gas and vapor (assumed value, 0.5 $cm^2\ sec^{-1}$)
E	Evaporation rate
g	Temperature gradient
k	Mass flow rate of vapor
k_T	Thermal-diffusion ratio
ℓ	Length of isothermal region
L	Length of sample-containing region (assumed value, 2.0 cm)
M	Molecular weight of vapor (assumed value, 200 g $mole^{-1}$)
n_v	Moles of vapor
n_c	Moles of carrier gas
N	Mole fraction of one component of binary-gas mixture in isothermal region
N'	Mole fraction of one component of binary-gas mixture in thermal-gradient region
N_o	Mole fraction of component in entering gas mixture
p	Partial pressure of vapor
P	System pressure (assumed value, 1.0 atm)
p_a	Actual partial pressure of vapor
p_m	Average partial pressure of vapor
p_o	Saturation vapor pressure
r	Radial distance from center line

Symbol	Definition
r_o	Radius of sample-containing region (assumed value, 0.5 cm)
R	Gas constant
t	Time
T	Absolute temperature (assumed value, 1000°K)
v	Flow velocity in volume units, $v = AV$
V	Linear flow velocity of gas mixture
x	Distance along tube from left to right (see Figs. 1 and 4)

INTRODUCTION

The transpiration method is one of the oldest and most versatile ways of studying heterogeneous equilibria involving gases. Thompson(1) gives the French chemist and physicist Regnault(2) credit for being, in 1845, the first to use this method. It is used primarily for measuring vapor and dissociation pressures, but it may be applied to gas-solid or gas-liquid equilibria in general. It is one of the few methods that can be used for measuring the pressure of a vapor in the presence of large concentrations of other gases. In valuable reviews, Kubaschewski and Evans,(3) Margrave,(4) and Richardson and Alcock(5) have discussed applications of the method and have described many of the experimental techniques that have been employed.

In the present review, diffusion and kinetic aspects of the transpiration method are discussed to show how they limit its usefulness, particularly in high-temperature chemistry. Also, certain aspects of the experimental techniques are discussed that may be helpful to the investigator in designing apparatus and conducting experiments. Finally, techniques are described by which the method may be used to establish the molecular formulas of vapor species.

GENERAL PRINCIPLES

In the transpiration method, a gas, which may be either inert or reactive, is passed over a condensed sample at a rate sufficiently low for equilibrium conditions to be established. The gas is collected at some point downstream from the sample and is analyzed to determine the vapor or dissociation pressures of components in the sample. The method is very useful for measuring vapor pressures and dissociation pressures in systems in which such pressures cannot be measured by more direct means.

APPARATUS

The essential features of the transpiration apparatus are illustrated in Fig. 1. The carrier gas, introduced at A, flows past the sample in an isothermal region, C. The constrictions at B and D minimize diffusion and heat loss. The equilibrium gas mixture emerging at E from the capillary (in some cases porous plugs have been used in place of capillaries) is collected at a point downstream and analyzed.

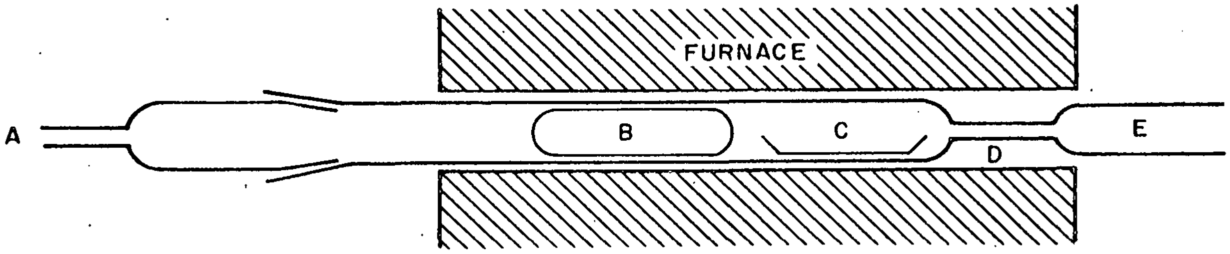

Fig. 1--Transpiration apparatus

The materials of construction are often dictated by the requirement that they be adequately strong at the temperature of interest and that they not react significantly with the sample or carrier gas. Glass and fused quartz have been extensively used, and an apparatus like that of Fig. 1 is readily constructed of these materials. Sense, Snyder, and Clegg,(6) and Popov, Kostyler, and Zubova(7) have used nickel and platinum, respectively, for work on fluorides. Bell, Merten, and Tagami,(8) using mullite in contact with chlorine gas at temperatures up to 1500°C, have found only slight attack on the mullite, and Fincham and Richardson(9) have successfully used alumina up to 1650°C in contact with platinum metal and gas mixtures containing H_2, CO_2, SO_2, and N_2.

Resistance-heated tube furnaces in conjunction with temperature controllers are commonly employed, and auxiliary heaters are frequently placed at the ends of the furnace to minimize temperature gradients. In vapor-pressure measurements, the capillary region is sometimes kept a few degrees hotter than the sample to prevent the condensation of vapor in the capillary.

TECHNIQUES AND APPLICATIONS

The transpiration method has been widely used for vapor-pressure measurements. In the usual experiment, an inert gas flows over the sample of interest; the vapor-laden gas passes through a capillary; the vapor condenses downstream in a cooler portion of the system; and the gas collects in a gas burette. The amount of material condensed is determined by chemical means, by the weight gain of the condenser, or by the weight loss of the sample. Typical of such measurements is the work of von Wartenberg,(10) who measured vapor pressures of lead, silver, and thallium in the range 800° to 1400°C. He passed measured quantities of hydrogen gas over metal samples held at a set temperature and determined the quantity of vapor transported by measuring the loss in weight of the sample.

Argon, nitrogen, and hydrogen are the most frequently used carrier gases. Since hydrogen gives a reducing atmosphere, it has often been used in measuring the vapor pressures of metals and alloys. Burmeister and Jellinek(11) used both hydrogen and nitrogen as carrier gases in measuring the vapor pressures of cadmium over Sn-Cd alloys and zinc over Sn-Zn alloys. As would be expected, they found vapor transfer by diffusion to be a more serious problem with hydrogen than with nitrogen.

Reactive carrier gases are often used to form species or to prevent dissociation of species being studied. Thus, Ackermann, et al.,(12) studied the vapor pressures of oxides of uranium, molybdenum, and tungsten using oxygen as a carrier. The vapor was collected in a condenser and the volume of gas flowed was measured with a wet-test meter. Gregory and MacLaren(13) used bromine as a carrier in studying the vapor pressure of iron bromide. They used a sensitive colorimetric technique to determine the amount of vapor condensed and were thus able to determine vapor pressures as low as 10^{-3} mm. The bromine was collected in potassium iodide solution, and the iodine liberated was titrated with thiosulfate.

Hydrogen sometimes behaves as a reactive gas; for example, Schafer and Klemm(14) found evidence for the existence of volatile hydrides of germanium and silicon. In their work apparent vapor pressures of germanium, silicon, tin, lead, and bismuth were determined by the transpiration method using either hydrogen or argon. The higher apparent pressures found for germanium and silicon in hydrogen were attributed to the formation of unstable volatile hydrides.

As will be shown in a later section, vapor species are sometimes identified by observing the effect of the variation in the partial pressure of a reactive carrier gas on the pressure of the vapor. The pressure of the reactive carrier is varied either by dilution with an inert gas or by changing the system pressure. Using the latter approach, Gregory and MacLaren(13) in work on iron bromides studied the effect of bromine pressure on the vapor pressure of the bromide. They used bromine as the carrier gas and varied the system pressure between 200 mm and 25 mm by controlling the rate of bromine flow into the system and also by operating the bromine supply at various temperatures; they were thus able to show that under their experimental conditions the principal vapor species was Fe_2Br_6.

Some investigators have passed an inert gas over a source of a reactive gas in a separate furnace and have allowed the mixture formed to serve as the carrier. Thus, Wilson and Gregory(15) in studies of the iron-chlorine system flowed argon over $CuCl_2$ in a separate furnace to obtain controlled mixtures of chlorine in argon. Cubicciotti,(16) in an investigation of the lower chlorides of bismuth, obtained controllable pressures of $BiCl_3$ by passing nitrogen over liquid $BiCl_3$ in a separate furnace.

In addition to its use for vapor-pressure measurements, the transpiration method has been used extensively for dissociation-pressure measurements. For example, Shchukarev, Kolbin, and Ryabov(17) measured the dissociation pressure of $RuCl_3$ in the range 500° to 900°C by flowing nitrogen over the substance. The nitrogen was collected in an inverted gas cylinder and the chlorine liberated by the chloride was absorbed in potassium idoide solution. Bell, Garrison, and Merten(18) made similar measurements on $RuCl_3$ using argon as the carrier gas. Gilbert and Kitchener(19) determined the partial pressure of cadmium over solid CdO between 880° and 1100°C. Nitrogen and oxygen were used as carrier gases, and the cadmium that was carried over into a condenser was dissolved in dilute HCl; the quantity was determined by electrodeposition. By comparing the results obtained using nitrogen with the results using oxygen, they deduced that vaporization occurs only through complete dissociation.

Gas mixtures are often used to obtain reactive gases at pressures that are too low for direct measurement. For example, in studies of cuprous chloride vapor, Brewer and Lofgren(20) used an HCl-H_2 mixture to vary the activity of chlorine. A mixture of the two gases, made up in pressure vessels, was passed over copper metal. The condensed vapor was analyzed chemically; the HCl was extracted with water and titrated; and the hydrogen was determined by difference. In using gas mixtures, the investigator must be sure that the addition of another component does not affect the activity of the condensed phase and also that thermal gradients do not cause unmixing of the gases (see "Thermal Diffusion"). For a valuable discussion of the use of gas mixtures, the reader is referred to Richardson and Alcock.(5)

MEASUREMENTS AND INTERPRETATION OF DATA

The data normally collected from a transpiration experiment are (1) the number of moles of each gaseous constituent, (2) the total pressure in the system, and (3) the experimental temperature. Various methods for determination of the gas composition are described in the previous section.

The total pressure is usually measured with a simple manometer, care being taken to ensure that the pressure is measured in the sample region and not before or after some constriction that might introduce a significant pressure drop. The range over which the system pressure is varied usually extends from an upper limit of 1 atm, or slightly above, down to about 0.1 atm. The upper limit is generally determined by the apparatus, which has rarely been designed for use at positive pressures. The lower limit is set by the increasing difficulties with gaseous-diffusion effects that are encountered as the pressure is lowered.

Temperatures are commonly measured by placing suitably calibrated thermocouples alongside the reaction tube or by inserting a thermocouple-well into the sample region. Even in the most carefully designed experiments, temperature uncertainties probably range from $\pm 1^{\circ}$ at 500°C to $\pm 4^{\circ}$ at 1500°C. At high temperatures, differences in temperature of several degrees may exist over short distances in a supposedly isothermal region; therefore, it is important to check the temperature in the reaction tube at the exact location of the sample. If care is taken to ensure that the arrangement is reproducible, this can be done in separate experiments.

From the data collected, the partial pressures of the various gases are calculated assuming ideal behavior. For calculating vapor pressures one uses the expression

$$p = \frac{n_v}{n_v + n_c} P , \qquad (1)$$

where p is the vapor pressure; n_v and n_c are the number of moles of vapor and associated carrier gas, respectively; and P is the total pressure. Of course, in order to calculate n_v from the analytical data, the molecular formula of the vapor species must be known. Methods for determining molecular formulas will be discussed in a following section.

In vapor-pressure work, the transpiration method is normally used over the range of about 10^{-5} to 0. 1 atm. The lower limit to the sensitivity of the method is set by the ability of the investigator to determine n_v. Runs of many hours duration are often used to increase the quantity of vapor transported, and the use of modern analytical tools can push the lower limit down to quite small values. Colorimetric and radiochemical methods of analysis are very helpful.

Extremely low dissociation pressures have been determined indirectly by flowing gas mixtures. For example, Darken and Gurry,(21) by flowing $CO-CO_2$ mixtures over iron oxide, were able to determine dissociation pressures as low as 10^{-14} atm for the oxide.

DIFFUSION AND KINETIC EFFECTS

Many users of the transpiration method have calculated apparent vapor pressures from expressions like Eq. (1) and have displayed the results as a function of flow rate in curves like that of Fig. 2 (see, for example, Richardson and Alcock$^{(5)}$). At low total flow the fraction $n_v/(n_v + n_c)$ becomes large, because vapor diffusion contributes significantly to n_v. At high flow rates $n_v/(n_v + n_c)$ becomes small, because kinetic limitations prevent saturation of the carrier gas.

Most investigators strive to select rates in the plateau region of Fig. 2, where the vapor pressure is independent of flow rate. Experiments performed in this region need no correction for diffusion or kinetic effects. The flow-rate range of the plateau region will vary according to the experimental setup and system studied. Flow rates reported in the literature are usually in the range 1 to 70 ml (STP)/min. By selecting a capillary of the proper dimensions in order to minimize diffusion effects and by selecting a sufficiently large sample surface area in order to saturate the gas rapidly, one can usually design experiments such that the plateau region extends over at least a threefold range of flow rate.

Some investigators fail to find a plateau region in which the vapor pressure is independent of flow rate; they find, instead, a continuous increase of vapor pressure at decreasing flow rates. This failure to find a plateau region is probably caused by improper design of the experiment; nevertheless, investigators sometimes attribute this behavior to incomplete saturation of the gas, and they extrapolate the data to zero flow rate to obtain the so-called true vapor pressure. The danger of such a procedure is that the flow-rate dependence may not be due to incomplete saturation but, rather, to diffusion effects or to temperature inhomogeneities in the sample region. In cases where the effect is caused by diffusion,

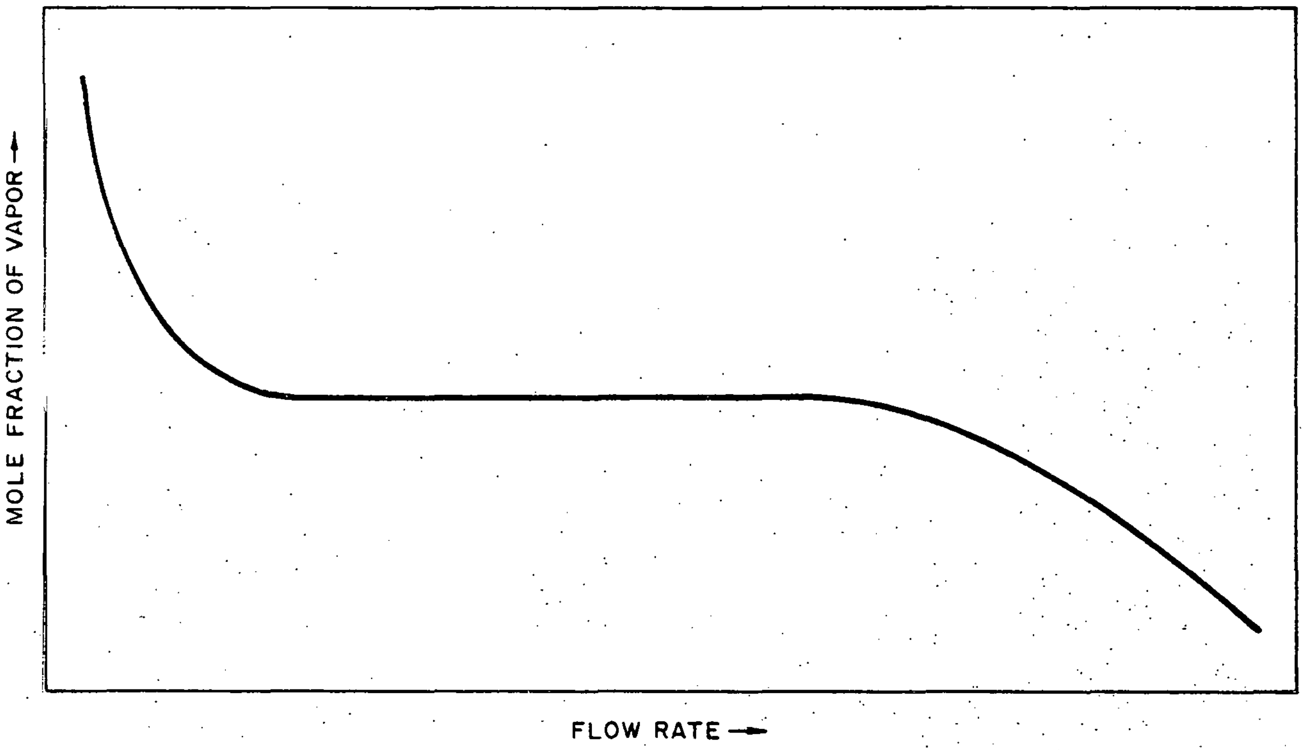

Fig. 2--Variation with the flow rate of mole fraction of vapor in effluent gas from transpiration experiment

extrapolation to a zero flow rate will give vapor pressures that are too high. This was pointed out by Braune(22) in commenting on the work of von Wartenberg.(10) The latter used hydrogen as a carrier gas in studies of the vapor pressure of metals and extrapolated his data to a zero flow rate. The vapor pressures that he reported are too high, undoubtedly because of diffusion effects that are especially pronounced when hydrogen is used as a carrier. In cases where failure to obtain a plateau region is caused by temperature inhomogeneities, it is clear that nothing is to be gained by extrapolating to a vapor pressure that does not apply to the measured temperature.

In the discussion that follows, both the diffusion and the saturation aspects of the transpiration method will be considered. On page ii are listed the symbols to be used, together with a set of assumed values (typical of those encountered in some of the authors' experiments), which will be used in sample calculations. Most of the calculations will apply specifically to the geometry of Fig. 1; however, extension to other simple geometries should be straightforward.

ORDINARY DIFFUSION

In an apparatus like that of Fig. 1, the vapor that enters the carrier gas in the sample region is most commonly removed by condensation just beyond the exit end of the capillary. Wagner and Stein(23) and Merten(24) have pointed out that under these circumstances the flow of vapor through the isothermal capillary can be written as the sum of a bulk flow and a diffusion term,

$$k = A\left(Vc - D\,\frac{dc}{dx}\right) . \tag{2}$$

At steady state, k must be constant throughout the length of the capillary, so Eq. (2) is readily integrated and

$$p = \frac{k}{v}\,\frac{RT}{M}\left[1 - \exp\left(-\frac{v\lambda}{DA}\right)\right] . \tag{3}$$

The constant of integration was evaluated for a capillary of length λ, with the assumption that the vapor is condensed immediately as it leaves the capillary (i. e., $c = 0$ at $x = 0$). The vapor is assumed to behave as an ideal gas. The exponential term in this equation results from the diffusion effect. Without it (i. e., for large v), Eq. (3) reduces to a form equivalent to Eq. (1),

$$p = \frac{k}{v} \frac{RT}{M} . \qquad (4)$$

For $v = 0$, Eq. (3) reduces to a diffusion equation.

Equation (3) has the form shown in Fig. 3, where k is represented as a function of v for constant p. In the straight-line portion of the curve, the amount of vapor transported is proportional to the flow rate, and the simple expressions of Eqs. (1) or (4) can be used directly to calculate p. The diffusion contribution, which is significant at low flow rates, vanishes as the flow rate is increased. Thus, the diffusion term is not simply additive, and the procedure used by some workers in which an experiment is performed at zero flow rate and the result subtracted from higher-flow-rate results is not valid.

Even if no straight-line relationship can be attained, it is possible in principle to determine both p and λ/DA from Eq. (3) if two experimental values for k as a function of v are available. In practice, this procedure will seldom be necessary, since it will usually be possible to design experiments in such a way that

$$\exp\left(-\frac{v\lambda}{DA}\right) << 1 . \qquad (5)$$

Thus, using the assumed values given in the Nomenclature,

$$\exp\left(-\frac{v\lambda}{DA}\right) < 0.01 , \qquad \text{for } v > 9 \times 10^{-3} \text{ cm}^3/\text{sec} .$$

Therefore, at flow rates higher than 9×10^{-3} cm^3/sec, the diffusion error involved in using Eqs. (1) or (4) would be < 1% under these conditions. For any pair of gases, D may be estimated by methods discussed by Reid and

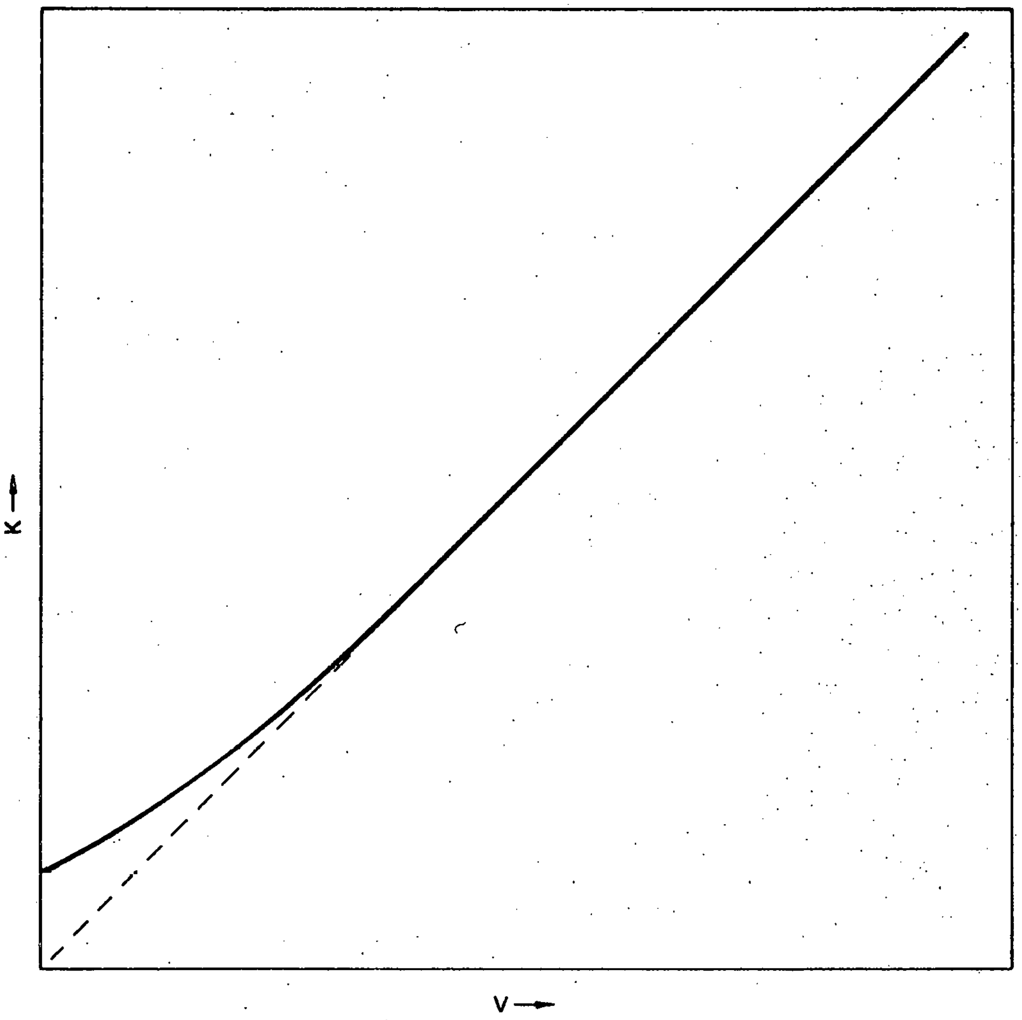

Fig. 3--Variation of vapor transport with gas flow rate

Sherwood.(25) Since D varies linearly with the reciprocal of the total pressure, the diffusion problem becomes more serious as the pressure is reduced.

Diffusion of vapor out of the sample region may also occur in the upstream direction. This will lead to an error in the same way as does downstream diffusion if the loss in weight of the sample is used to determine n_v (see Eq. (1)). It may lead to an error in any case if the diffusion rate is large enough to cause nonequilibrium conditions (undersaturation) in the sample region. To minimize this error and to facilitate thermal insulation of the sample from the cold inlet region, it is customary to constrict the inlet passage to the sample region as well as the outlet.

THERMAL DIFFUSION

The diffusion effect described above results from the removal of one component from the gas stream at a point close to the sample region. A somewhat similar problem may arise from diffusion in thermal gradients. For instance, if there is no condensation of a gaseous component on reaching the cold region (e. g. , in a dissociation-pressure measurement) there may still be a diffusive flow caused by a temperature gradient in the exit portion of the apparatus. If a mixed carrier gas is employed, it may unmix in the thermal gradient. Richardson and Alcock(5) have presented a useful discussion of thermal unmixing during equilibrium measurements, including a compilation of some experimental results on the effect.

One can gain further insight into the problem of thermal diffusion by examining the flow equations in some detail. Let us consider an experiment in which a mixture of two gases is passed from left to right through an apparatus that has a temperature profile as indicated in Fig. 4a. Let N be the mole fraction of one component in a binary gas mixture and N_o its mole fraction in the entering gas. At steady state, the gas leaving the apparatus (e. g. , by bubbling into a collection vessel) must also have $N = N_o$. This fixes the end points of the mole-fraction profile shown in Fig. 4b.

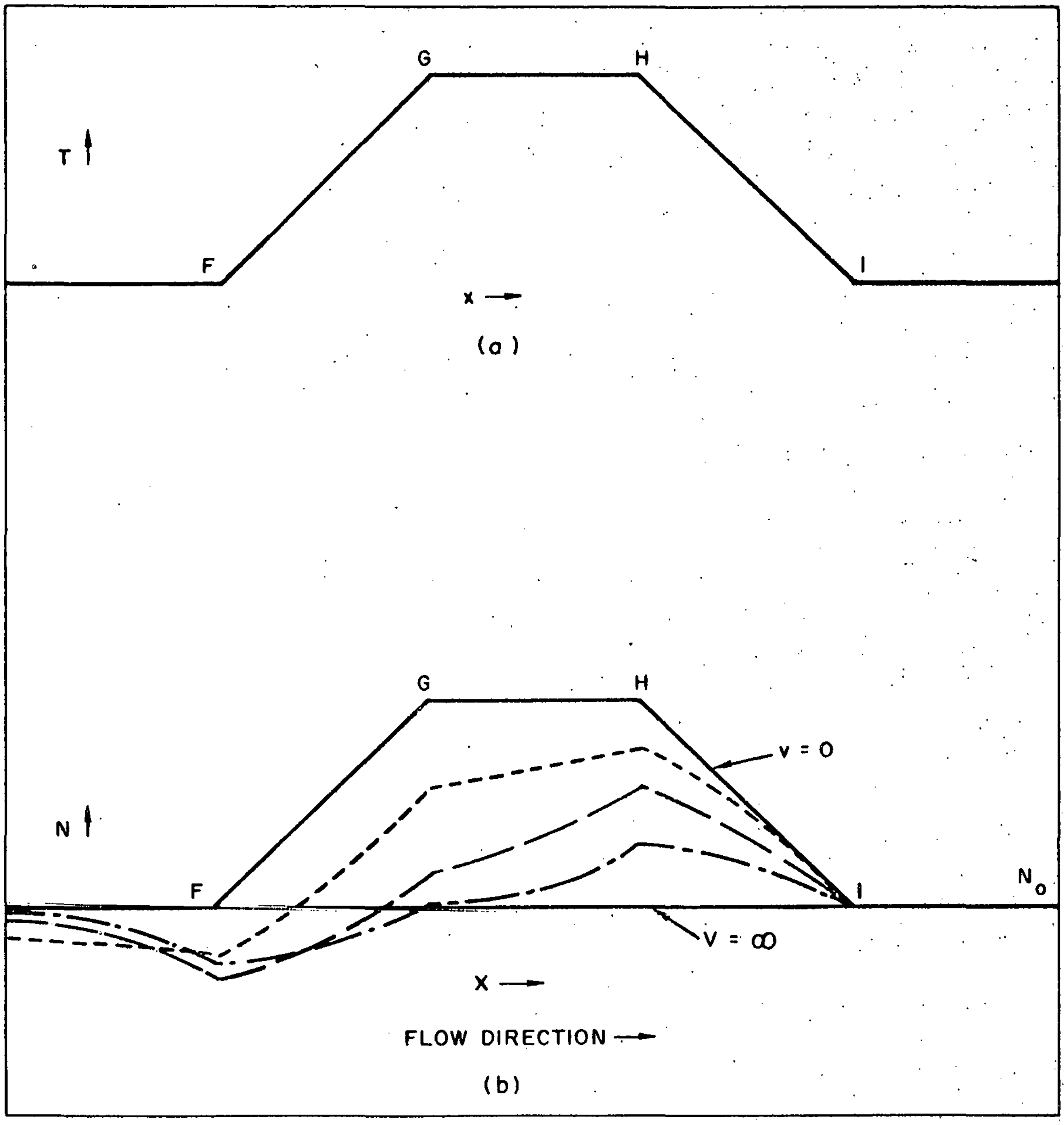

Fig. 4--(a) Temperature profile; (b) mole-fraction profile as flow velocity of gas mixture is varied

Equation (2) applies in the isothermal regions and may be rewritten as

$$VN_o = VN - D \frac{dN}{dx} . \tag{6}$$

In converting Eq. (2) to Eq. (6), ideal-gas behavior was assumed. From Eq. (6), it is apparent that for

$$N > N_o, \ \frac{dN}{dx} > 0 ,$$

and for

$$N < N_o, \ \frac{dN}{dx} < 0 ,$$

in the isothermal regions. As a result, N must equal N_o from point I (in Fig. 4b) to the exit, and N must be nearer N_o at point G than at point H. If the two temperature-gradient regions are sufficiently far apart, there will be a region between, far from the second of these disturbances, where $dN/dx \cong 0$ and, therefore, $N = N_o$.

In the isothermal regions upstream from the thermal-gradient regions, integration of Eq. (6) gives

$$N_1 = N_o + (N_2 - N_o) \exp\left(\frac{Vx}{D}\right) , \tag{7}$$

where x is to be measured from left to right from the beginning of the thermal-gradient region (e. g., in Fig. 4, x = 0 at H, and $x = -\ell$ at G). The constant of integration is evaluated for the boundary condition $N = N_2$ at $x = 0$. The value of N_2 must be obtained by solving the flow equations within the thermal-gradient regions.

In the thermal-gradient regions (F to G, and H to I, in Fig. 4a),

$$VN_o \doteq VN' - D \frac{dN'}{dx} + D k_T \frac{1}{T} \frac{dT}{dx} , \tag{8}$$

which is simply Eq. (6) with an added thermal diffusion term. Integration of Eq. (8) is complicated by the fact that V is directly proportional to T, D varies approximately as $T^{1.75}$, and k_T is, in general, strongly dependent on N' and slightly dependent on T. Darken and Gurry(21) obtained an approximate solution of Eq. (8) by assuming dT/dx to be constant, V to be proportional to T, D to be proportional to T^2, and k_T to be independent of N' and T. They thus arrived at the differential equation

$$\frac{dN'}{d\ln T} = k_T + \frac{V_o T_o}{g D_o} (N' - N_o) , \tag{9}$$

where V_o and D_o are values of V and D at T_o. By integration of Eq. (9), they obtained

$$\frac{k_T + \frac{V_o T_o}{g D_o} (N_2' - N_o)}{k_T + \frac{V_o T_o}{g D_o} (N_1' - N_o)} = \left(\frac{T_2}{T_1}\right)^{\frac{V_o T_o}{g D_o}} . \tag{10}$$

The constant of integration was evaluated for $N' = N_2$ at $T = T_2$. Equation (10) reduces to

$$k_T = \frac{V_o T_o}{g D_o} (N_o - N_1') , \tag{11}$$

when T_2/T_1 and/or V_o are large.

Darken and Gurry(21) measured the thermal separation of CO-CO_2 mixtures at various flow rates and used Eq. (11) to calculate a value for k_T. The value obtained agreed reasonably with experimental values for similar gases, and they thus concluded Eq. (11) to be an adequate interpretation of the thermal-diffusion problem.

Other approximate solutions to Eq. (8) can be otained by using different simplifying assumptions. Thus, the thermal diffusion factor,* α, which

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*Values of α for gas mixtures may be found in Hirschfelder, Curtis, and Bird,(26) Grew and Ibbs,(27) and Chapman and Cowling,(28) as well as in other texts. For our purposes, it will often suffice either to calculate the rigid-sphere value of α or to estimate it from the graphical presentation of Grew and Ibbs. (It should be noted that in Fig. 7 of Grew and Ibbs the abscissa is actually 2Σ, not Σ.) The true value of α is, in general, less is more justifiably assumed independent of N than is k_T, may be introduced into Eq. (9) by using the equality

$$k_T = \alpha N'(1 - N') .$$

The resulting differential equation can be readily integrated, but the solution, though more accurate than Eq. (10), is rather unwieldy. For dilute mixtures, $1 - N' \cong 1$, and k_T may be replaced in Eq. (9) by $\alpha N'$. Integration of the resulting differential equation yields a useful solution.

The solutions to Eq. (8) that have been mentioned, although implicit in x, since dT/dx was assumed constant, give N' as a function of T. A convenient expression of N' as a function of x can be obtained from Eq. (8) by assuming dT/dx to be constant and V, D, and k_T each to be proportional to T and independent of N'. The resulting differential equation is:

$$\frac{dN'}{dx} = -\frac{V_o N_o}{D_o} + \frac{k_{T_o} g}{T_o} + \frac{V_o N'}{D_o} , \tag{12}$$

where V_o, D_o, and k_{T_o} are values of V, D, and k_T at T_o. Integration yields

$$N_1' = -\frac{a}{b} + \left(\frac{a}{b} + N_2'\right) \exp b(x - d) , \tag{13}$$

where

$$a = -\frac{V_o N_o}{D_o} + \frac{k_{T_o} g}{T_o} ,$$

and

$$b = \frac{V_o}{D_o} .$$

The constant of integration was evaluated for $N' = N_2'$ at $x = d$. When the

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than the rigid sphere value, but in most cases that have been studied, the two are the same within an order of magnitude above room temperature.

exponential term is small, Eq. (13) reduces to

$$N_1' = -\frac{a}{b} = N_o - \frac{k_{T_o} D_o g}{V_o T_o}, \qquad (14)$$

which is identical to Eq. (11).

It is now possible to calculate the complete mole-fraction profile of the experiment. As the first step, either Eq. (10) or Eq. (13) may be used to evaluate N' over the interval H to I in Fig. 4b. In this calculation, N_2' is taken to be N_o (that this is true was shown above), and N_1' is evaluated at x (or at T_1, depending on the equation used). The value of N_1' obtained at x = 0 (or at T_1, where x = 0) is used in Eq. (7) as N_2, and the mole fraction N_1 at point G is calculated. The whole procedure may be repeated between point G and the inlet to the apparatus by using the appropriate boundary conditions; thus, the complete profile for the experiment is calculated. The profiles shown in Fig. 4b, which were calculated in this manner for a set of assumed values (Eq. (13) was used in the thermal-gradient regions), are typical of the shapes obtained as the flow rate is varied. In practical cases, the assumptions made regarding V, D, k_T, and dT/dx are not entirely valid; still, the general features of the profile will be preserved and the equations can be used for semiquantitative calculations.

In a transpiration experiment, it is desirable to have $N = N_o$ at the sample position. It is clear from either Eq. (11) or (14) that this will be true if

$$\frac{k_T D_o g}{V_o T_o} << 1 \qquad (15)$$

at all points in the second temperature-gradient region. Thermal-diffusion effects are thus minimized at high flow rates in the temperature gradient. As mentioned above, these effects may also be diminished by increasing the effective distance between the sample and the second temperature-gradient region.

In the worst case, the thermal-diffusion effect might be so severe that the concentration (or mole fraction) of one component goes to zero at the entrance to the second temperature gradient. Should this happen, the situation in the isothermal region would be analogous to that discussed earlier for vapor condensation; the limitations of Eq. (5) could then be applied. Thus, the isothermal constriction used to suppress ordinary diffusion will also suppress thermal diffusion no matter how serious a concentration gradient may be set up in the temperature-gradient region beyond. It is noteworthy that nothing is to be gained by increasing the effective length of the isothermal region upstream from the sample or by increasing V (for example, by use of a constriction) in the first temperature-gradient region.

It is of interest to test the usefulness of Eq. (15) with some experimental results. Darken and Gurry(21) found that in their apparatus the thermal separation of CO-CO_2 mixtures was less than 0.05% CO at the center of the furnace, i.e., $N_1' - N_o < 0.0005$ for flow rates in excess of 0.6 cm/sec measured at room temperature. Using their numerical values, $D_o = 0.14\ cm^2/sec$, $k_T = 0.042$, $g = -60^o/cm$, and $T_o = 273^oK$, in Eq. (15), it is estimated that $N_1' - N_o < 0.0005$ for $V > 2.6$ cm/sec. The calculated value is considerably higher than the experimental value; however, this is not unexpected since Darken and Gurry found that convection currents existing in their apparatus minimized thermal-diffusion effects.

It should be emphasized again that Eqs. (10) and (13) are exact solutions only for special cases and that quantitative agreement of the integrated equations with experimental data is not to be expected. Nevertheless, the equations have considerable usefulness in the designing of experiments.

SATURATION EFFECTS ASSUMING CONSTANT VAPOR PRESSURE AT SAMPLE SURFACE

Just as the diffusion problems discussed above set some lower limits on the flow rates that may be used in the transpiration method, other kinetic considerations set an upper limit on these rates. At high flow rates, saturation of the carrier gas may not be achieved because of incomplete mixing in the gas stream or insufficiently rapid evaporation of the sample. In the following discussion, the gas-mixing problem will be treated assuming laminar flow and constant vapor pressure at the sample surface. It will be convenient for mathematical reasons to assume that the sample is in the form of a tube.

The formulism for discussing the gas-mixing problem in the experimental geometry already described is readily written down. The velocity profile in laminar flow through a tube is parabolic, so that

$$V = K(r_o^2 - r^2) . \tag{16}$$

The constant K can be evaluated by integrating the flow velocity over the cross-sectional area and setting it equal to the total volume flow rate. The result is

$$V = \frac{2v}{\pi r_o^4} (r_o^2 - r^2) . \tag{17}$$

At steady state, the vapor concentration at any point in the tube will be constant, and

$$\frac{dc}{dt} = \left(\frac{dc}{dt}\right)_f + \left(\frac{dc}{dt}\right)_d = 0 , \tag{18}$$

where $(dc/dt)_f$ is the rate of change in concentration due to flow of the vapor-laden gas into the region of interest, and $(dc/dt)_d$ is the change due to diffusion into the region. Then,

$$\left(\frac{dc}{dt}\right)_f = -V \frac{\partial c}{\partial x}$$

and

$$\left(\frac{dc}{dt}\right)_d = D \frac{\partial^2 c}{\partial x^2} + \frac{D}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r}\right) .$$

Substituting these equations and Eq. (17) into Eq. (18), one obtains

$$\frac{2v}{\pi r_o^2}\left[1-\left(\frac{r}{r_o}\right)^2\right]\frac{\partial c}{\partial x} = D\left[\frac{\partial^2 c}{\partial x^2}+\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right)\right]. \tag{19}$$

A suitable set of boundary conditions for the present problem would include the condition that the vapor concentration at the surface is the same as the saturation concentration and is independent of the distance along the tube. The solution of Eq. (19) with this boundary condition is difficult, but fortunately an analogous heat-transfer problem has been solved,[*] and the desired results are obtained by making suitable substitutions in equations given by Jakob.(29) The deviation of the average vapor concentration from saturation is given by

$$1-\frac{p_m}{p_o} = 0.820\ e^{-m_o x} + 0.0972\ e^{-m_1 x} + 0.0135\ e^{-m_2 x} \ldots , \tag{20}$$

where p_m is the average partial pressure of the vapor in the gas flowing through a cross section of the sample tube at a distance x from its leading edge, p_o is the saturation partial pressure, and

$$m_o = 3.660\ \frac{\pi D}{v} ,$$

$$m_1 = 22.2\ \frac{\pi D}{v} ,$$

$$m_2 = 53.0\ \frac{\pi D}{v} .$$

Neglecting all terms but the first, one can establish as a criterion for good gas mixing

$$1-\frac{p_m}{p_o} \cong 0.820 \exp\left(\frac{-3.66\pi DL}{v}\right) < 0.1 . \tag{21}$$

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[*] The analogous problem is that of heat transfer to a fluid flowing through a cylindrical duct whose surface temperature is uniform.

The value 0.1 is arbitrary. Equation (21) reduces to

$$v < \left| \frac{3.66\pi DL}{\ln 8.20} \right| , \tag{22}$$

and this value sets one upper limit on the usable flow rates. Using the assumed values shown in the Nomenclature in this expression, it is estimated that for apparatus of the type shown in Fig. 1, gas mixing will be a problem only if $v > 5.5\ \mathrm{cm}^3/\mathrm{sec}$.

SATURATION EFFECTS ASSUMING CONSTANT EVAPORATION RATE

In the above treatment the gas-mixing problem was considered assuming the carrier gas in direct contact with the wall to be saturated with vapor. In the following treatment, the case is considered in which the gas mixing is good across the diameter of the sample tube and the evaporation rate is limiting. The treatment will be most accurate in geometries where $L \gg r_o$. Again, the sample is assumed to be in the form of a hollow tube. The effects of longitudinal diffusion will be neglected, since the interest is now primarily in relatively high flow rates where the contribution from longitudinal diffusion will be small.

The net rate at which vapor comes off a unit area of sample may be assumed to follow the Langmuir equation, so that

$$E = \alpha_e (p_o - p_a) \left(\frac{1}{2\pi RTM} \right)^{1/2} , \tag{23}$$

where α_e is the evaporation coefficient and E is expressed in molar units. The increase in partial pressure as the sample moves down the tube will be

$$\frac{dp}{dx} = RT \frac{dc}{dx} = RT \frac{2\pi r_o E}{v} , \tag{24}$$

and, since $p = 0$ at the inlet end of the sample (i.e., at $x = 0$), it can readily be shown that

$$\frac{p_{a_L}}{p_o} = 1 - \exp \left[-\alpha_e \left(\frac{2\pi RT}{M} \right)^{1/2} \frac{r_o L}{v} \right] , \tag{25}$$

where p_{a_L} is the partial pressure of vapor at the outlet end (i.e., at $x = L$). For $p_{a_L} \cong p_o$, it is necessary that the absolute value of the exponent be large compared with unity, i. e.,

$$v << \alpha_e r_o L \left(\frac{2\pi RT}{M} \right)^{1/2} . \tag{26}$$

In general, this evaporation-rate limitation will be encountered first for samples of small area or small evaporation coefficient, while the gas-mixing effects previously discussed set the upper limit on usable flow rates for samples of large area or large evaporation coefficient. When either of these two limitations is encountered, the observed apparent pressures become dependent upon sample area and geometry. In most equilibrium measurements made by this technique, these last parameters are not closely controlled, and it is to be expected that, at flow rates where appreciable deviations from equilibrium values are observed, there will also be poor reproducibility between experiments.

Using the assumed values shown in the Nomenclature in Eq. (26), it is estimated that the evaporation rate will be a problem unless

$$v << 5.1 \times 10^4 \alpha_e \quad \text{cm}^3/\text{sec} .$$

Thus, at a typical experimental flow rate of the order of 0.01 cm^3/sec, saturation should be achieved unless α_e is of the order of 10^{-6} or smaller.

IDENTIFICATION OF VAPOR SPECIES

As mentioned above, knowledge of the molecular formula of the vapor species is necessary in interpreting data from vapor-pressure measurements using the transpiration method. Vapor-density, mass-spectrometric, and optical measurements are among the auxiliary techniques that can be used for this purpose. In many cases, as the following examples will show, the transpiration method itself can aid in establishing the identity of vapor species.

One technique is to vary the activity of a reactive gas. Brewer and Lofgren(20) used this approach in studies of the following equilibrium at 988° to 1340°K:

$$xCu(s) + yHCl(g) = Cu_x\,Cl_y(g) + \frac{y}{2}\,H_2(g) .$$

They passed various mixtures of H_2 and HCl over the copper and, from a plot of log $(xp_{Cu_x\,Cl_y})$ versus log $(p_{HCl}/p_{H_2}^{1/2})$, found y = 3. This result combined with results of other studies showed the vapor species to be Cu_3Cl_3. In similar studies, Cubicciotti(16) was able to show the vapor species in equilibrium with Bi(ℓ) and $BiCl_3(g)$ to contain one chlorine atom per molecule. In his work, the activity of $BiCl_3(g)$, carried in a nitrogen stream, was varied.

In some cases, binary vapor species can be fully identified by these methods. Consider, for example, the following equilibria:

$$xM(s) + \frac{y}{2}\,X_2(g) = M_xX_y(g) \qquad (27)$$

and

$$xMX_z(s\ or\ \ell) + \frac{y - zx}{2}\,X_2(g) = M_xX_y(g) , \qquad (28)$$

where, for purposes of discussion, M is considered to be a metal and X_2 a halogen gas. The system is such that both metal and condensed halide are stable over a portion of the halogen gas-pressure and temperature range that is available to the investigator. From the equilibrium constant for Eq. (27) is obtained

$$\log p_{M_xX_y} = \frac{y}{2} \log p_{X_2} + \log K .$$

A similar expression is obtained for Eq. (28). From a $\log p_{M_xX_y}$ versus $\log p_{X_2}$ plot, where the metal is the condensed phase, y/2 is evaluated; and from a similar plot, where the condensed halide is the condensed phase, (y - zx)/2 is evaluated. In general, the value of z, i.e., the identity of the condensed compound, is known or can be evaluated from other studies; thus, both x and y can be established and the vapor species can be identified unambiguously. Figure 5 shows isotherms obtained at 700° and 800°C by Bell, Garrison, and Merten,(30) who used this approach in identifying $RuCl_4$ as an important vapor species in the ruthenium-chlorine system at high temperature. It is readily seen that $y/2 \cong 2$, that $(y - zx)/2 \cong 0.5$ ($z = 3$ from other studies), and, therefore, that $y = 4$ and $x = 1$. Similarly, Schäfer and Heitland,(31) who worked in the range of 900° to 1200°C, identified IrO_3 as a vapor species in the iridium-oxygen system.

Alcock and Hooper(32) describe another technique for fully identifying binary vapor species. They consider equilibria of the type

$$xM(s) + y/2\, O_2(g) = M_xO_y(g) .$$

The equilibrium constant for this reaction is

$$K = \frac{p_{M_xO_y}}{p_{O_2}^{y/2}\, a_M^x} ,$$

where a_M is the activity of the metal M. Values for x and y are obtained

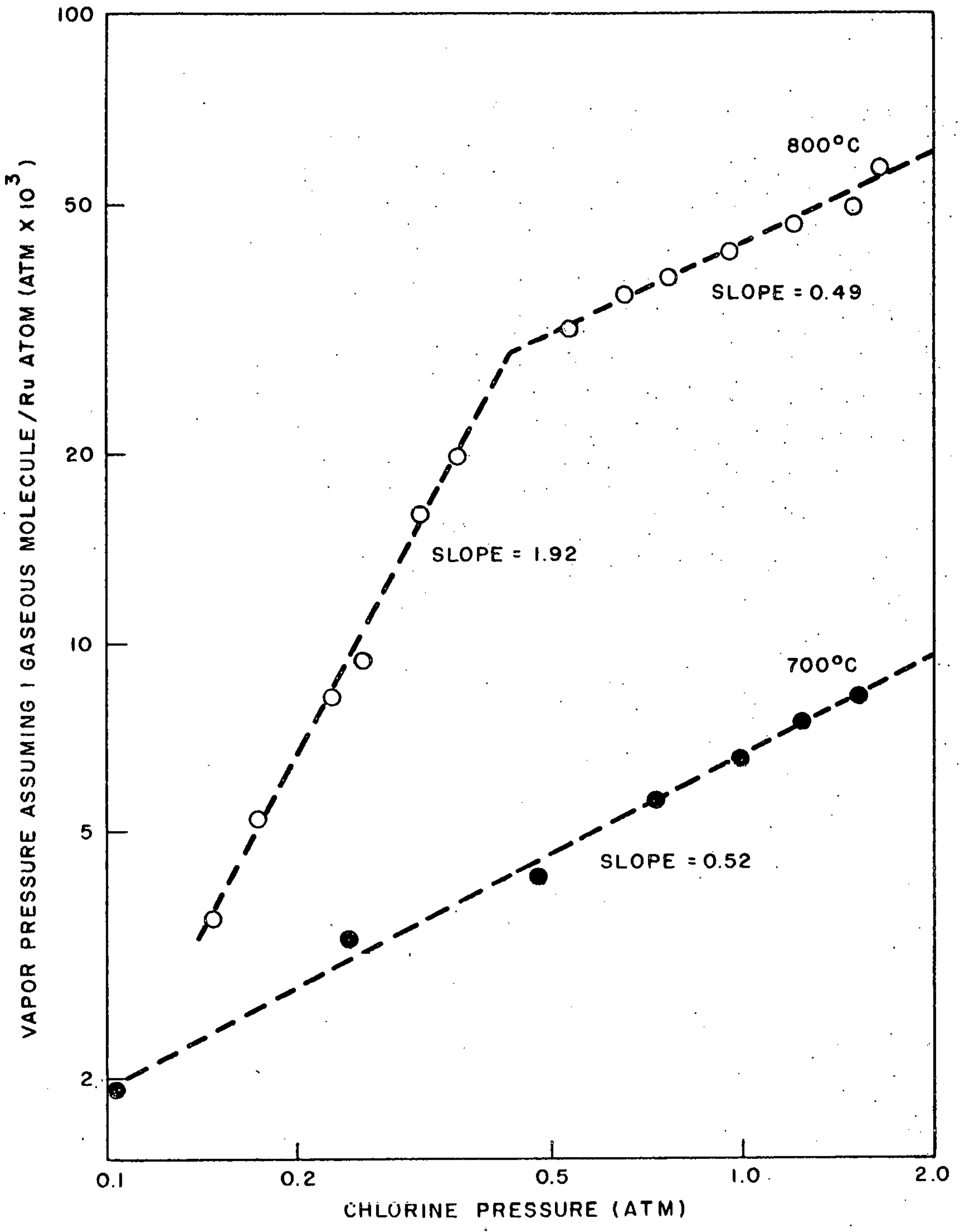

Fig. 5--Effect of chlorine pressure on vapor pressure at 700° and 800°C in ruthenium-chlorine system

by studying independently the effect of oxygen pressure and the effect of metal activity on the vapor pressure. Alcock and Hooper applied this technique to the platinum-oxygen system; they dissolved the platinum in gold, measured the vapor pressure of gold over the alloy, and from the result calculated the platinum activity by means of the Gibbs-Duhem relationship.

Sense, <u>et al</u>.,(33) used the transpiration method to study the vapor pressures of mixed fluoride systems and were able to show the existence of complex vapor species, such as $NaZrF_5$. Their analysis treats the mixture of two fluorides as a binary system, and they consider vaporization reactions of the following type:

$$xA(soln) + yB(soln) = A_xB_y(g) ,$$

where A_xB_y represents a gaseous metal complex in equilibrium with the metal fluorides A and B in solution. The vapor-phase equilibrium,

$$xA(g) + yB(g) = A_xB_y(g) ,$$

must of course be satisfied over solutions of all compositions; and from the equilibrium constant for this reaction one may write, assuming ideal gases,

$$\frac{dp_{A_xB_y}}{dN} = Kp_A^x \, yp_B^{y-1} \left(\frac{dp_B}{dN}\right) + Kp_B^y \, xp_A^{x-1} \left(\frac{dp_A}{dN}\right) ,$$

where N is the mole fraction of A in the condensed solution. The Gibbs-Duhem equation,

$$\frac{dp_B}{dN} = - \frac{N}{1 - N} \frac{p_B}{p_A} \frac{dp_A}{dN} ,$$

relates the two differentials on the right, and one can show that $p_{A_xB_y}$ has a maximum at $N = x/(x + y)$, i.e., when the liquid and vapor have identical compositions. Thus, from observed maxima in their vapor-pressure curves, Sense, et al.,(33) were able to obtain empirical formulas for the various metal complexes. Of course, as they pointed out, the transpiration method provides no information regarding the polymeric state of these vapors.

When the condensed phase of the system being studied melts in the temperature range available to the investigator, information regarding the polymeric state of a gaseous species may be obtained in another way. Consider the following vaporization and fusion reactions and related changes in heat content:

$$xM(\ell) = M_x(g) \qquad \Delta H_1 \;,$$

$$xM(s) = M_x(g) \qquad \Delta H_2 \;,$$

$$M(s) = M(\ell) \qquad \Delta H_3 \;.$$

The changes in heat content are related by the following expression:

$$\Delta H_3 = \frac{\Delta H_2 - \Delta H_1}{x} \;.$$

The values of ΔH_1 and ΔH_2 are determined from the temperature dependence of vapor-pressure data measured at temperatures above and below the melting point; and, providing ΔH_3 can be either estimated or determined independently, the value of x may be evaluated.

As a final note, it should be pointed out that there is no a priori way of determining the molecular formula of a vapor species from an analysis of the condensate in a transpiration experiment. Such a procedure overlooks polymeric vapor species and dissociative evaporation. In the authors' work on ruthenium chlorides,(30) the condensate was always $RuCl_3$, even when the principal vapor species was the tetrachloride; thus, even the empirical formula of the vapor species may differ from that of the condensate.

REFERENCES

1. Thomson, G. W , "Determination of Vapor Pressure," in Arnold Weissberger (ed.), *Technique of Organic Chemistry*; Vol. I--*Physical Methods of Organic Chemistry*, 3d. ed., Part I, Interscience Publishers, Inc., New York, 1959, pp. 401-522.
2. Regnault, H V., *Ann. Chim.*, Vol. 15, 129, 1845.
3. Kubaschewski, O., and E. L. Evans, *Metallurgical Thermochemistry*, 3d ed. (rev.), Pergamon Press, New York, 1958.
4. Margrave, J L., "Vapour Pressure," in J. O'M. Bockris (ed.), *Physicochemical Measurements at High Temperatures*, Academic Press, New York, 1959, pp. 225-246.
5. Richardson, F. D., and C. B. Alcock, "Chemical Equilibria," in J. O'M. Bockris (ed.), *Physicochemical Measurements at High Temperatures*, Academic Press, New York, 1959, pp. 135-170.
6. Sense, K. A., M. J. Snyder, and J. W. Clegg, "The Vapor Pressure of Beryllium Fluoride," *J. Phys. Chem.*, Vol. 58, 1954, p. 223.
7. Popov, M. M., F. A. Kostylev, and N. V. Zubova, "Vapor Pressure of Uranium Fluoride," *Zuhr. Neorg. Khim.*, Vol. 4, 1959, p. 770.
8. Bell, Wayne E., Ulrich Merten, and M. Tagami, "The Palladium-Chlorine System at High Temperatures," *J. Phys. Chem.*, Vol. 65, 1961, p. 510.
9. Fincham, C. J. B., and F. D. Richardson, "The Behavior of Sulfur in Silicate and Aluminate Melts," *Proc. Roy. Soc. (London)*, Vol. A223, 1954, p. 40.
10. Von Wartenberg, H., "Vapor Pressure of Metals," *Z. Elektrochem.*, Vol. 19, 1913, p. 482.
11. Burmeister, E., and K. Jellinek, "Vapor Pressure and Activities of Several Binary Alloys," *Z. physik. Chem.*, Vol. A165, 1933, p. 121.
12. Ackermann, R. J., R. J. Thorn, Carl Alexander, and Marvin Tetenbaum, "Free Energies of Formation of Gaseous Uranium, Molybdenum and Tungsten Trioxides," *J. Phys. Chem.*, Vol. 64, 1960, p. 350.
13. Gregory, N. W., and R. O. MacLaren, "Vaporization Reactions: The Iron-Bromine System," *J. Phys. Chem.*, Vol. 59, 1955, p. 110.
14. Schäfer, R., and W. Klemm, "Behavior of Metalloids Toward Hydrogen at High Temperatures," *J. prakt. Chem.*, Vol. 5, 1958, p. 233.

15. Wilson, L. E., and N. W. Gregory, "Vapor-Solid Equilibria in the Iron-Chlorine System," J. Phys. Chem., Vol. 62, 1958, p. 433.

16. Cubicciotti, D., "The Thermodynamic Properties of BiCl Gas," J. Phys. Chem., Vol. 64, 1960, p. 791.

17. Shchukarev, S. A., N. I. Kolbin, and A. M. Ryabov, "Dissociation and Sublimation of Ruthenium Trichloride," Zuhr. Neorg. Khim., Vol. 3, 1958, p. 1721.

18. Bell, W. E., M. C. Garrison, and Ulrich Merten, "The Dissociation Pressure of Ruthenium Trichloride," J. Phys. Chem., Vol. 64, 1960, p. 145.

19. Gilbert, I. G. F., and J. A. Kitchener, "The Dissociation Pressure of Cadmium Oxide," J. Chem. Soc., 1956, p. 3919.

20. Brewer, L., and N. L. Lofgren, "The Thermodynamics of Gaseous Cuprous Chloride, Monomer and Trimer," J. Am. Chem. Soc., Vol. 72, No. 7, 1950, p. 3038.

21. Darken, L. S., and R. W. Gurry, "The System Iron-Oxygen: I. The Wüstite Field and Related Equilibria," J. Am. Chem. Soc., Vol. 67, No. 8, 1945, p. 1398.

22. Braune, H., "Experimental Determination of the Vapor Pressure Curves of Liquid Cadmium and Zinc," Z. anorg. allgem. Chem., Vol. 111, 1920, p. 109.

23. Wagner, C., and V. Stein, "Investigation of the Volatility of Chromium Halides," Z. Physik. Chem., Vol. 192, 1942, p. 129.

24. Merten, Ulrich, "Diffusion Effects in the Transpiration Method of Vapor Pressure Measurement," J. Phys. Chem., Vol. 63, 1959, p. 443.

25. Reid, R. C., and T. K. Sherwood, The Properties of Gases and Liquids: Their Estimation and Correlation, Chemical Engineering Series, McGraw-Hill Book., Ltd., New York, 1958.

26. Hirschfelder, J. O., C. F. Curtis, and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley and Sons, New York, 1954.

27. Grew, K. E., and T. L. Ibbs, Thermal Diffusion in Gases, University Press, Cambridge, 1952.

28. Chapman, S., and T. G. Cowling, The Mathematical Theory of Non-uniform Gases, University Press, Cambridge, 1952.

29. Jakob, Max, Heat Transfer, Vol. I, John Wiley and Sons, New York, 1949, p. 451 ff.

30. Bell, W. E., M. C. Garrison, and U. Merten, "Thermodynamic Properties of Gaseous Ruthenium Chlorides at High Temperatures," J. Phys. Chem., Vol. 65, 1961, p. 517.

31. Schäfer, H., and H. J. Heitland, "Equilibrium Measurements in the System Iridium-Oxygen," Z. anorg. u. allgem. Chem., Vol. 304, 1960, p. 249.

32. Alcock, C. B., and G. W. Hooper, "Thermodynamics of the Gaseous Oxides of the Platinum-Group Metals," Proc. Roy. Soc. (London), Vol. A254, 1960. p. 551.

33. Sense, K. A., C. A. Alexander, R. E. Bowman, and R. B. Filbert, Jr., "Vapor Pressure and Derived Information of the Sodium Fluoride-Zirconium Fluoride System," J. Phys. Chem., Vol. 61, 1957, p. 337.