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An experimental technique employing a moveable Mach-Zender interferometer for measuring composition profiles in the gas phase of an Arnold diffusion cell has been developed. The experimental apparatus included a specially built cell having a pair of glass sides to allow continuous detection of the refractive index. With the integrated apparatus, the composition profiles of several diffusing binary gas systems were accurately measured.

From these composition profiles and measurements of the accompanying mass flux, the terms in Fick's law of diffusion were calculated. This allowed a direct determination of diffusivity at various system compositions. The variations of binary molecular diffusivity with composition for benzene-nitrogen and chloroform-nitrogen were calculated and compared to previous work.

Higher than expected mass fluxes were observed leading to speculation that a perturbed diffusion process was being observed.

Nevertheless, it was concluded that this use of an optical interferometer to experimentally measure gas phase concentration profiles is practical and accurate.

Determination of Concentration Gradients in a Diffusing Binary Gas System by Optical Interferometry

by

Donald Kenneth Waller

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Any task undertaken by an individual must include the efforts of countless others in order to be successful. Realization of this situation and knowledge that the value of any accomplishment is not an absolute thing, but ultimately is measured by its value to other people, forms the underlying basis for this particular project.

Of the many who devoted their time, particular appreciation for their contributions must be noted for the advisor on this project, Dr. Robert V. Mrazek, and the combined staff of the Department of Chemical Engineering. My association with the staff and other students was, and always will be, of lasting benefit.

Beyond those most immediately associated with this project stand a multitude of persons; former supervisors, professional colleagues, friends, and family, to whom I am indebted for making my graduate experience possible. Lastly, I wish to express a thorough and lasting acknowledgement to the citizens of Oregon who have provided the facilities and financial support which made this project feasible. To call Oregon home is a rare and honored privilege.

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INTRODUCTION

One phenomenon dealt with extensively in chemical engineering practice is diffusion, the tendency of solutions to move from localized inhomogeneity toward a uniform composition. Thorough analysis of this phenomenon leads to the conclusions that it is a molecular event and, in the absence of external forces, is spontaneous. The causes of the diffusion phenomenon and precise description of it are the subjects of extensive chemical engineering effort. Indeed, proper application and control of mass transfer through diffusion form one of the basic processes of the chemical industries.

Movement of a molecular specie undergoing diffusion constitutes a mass flux. Although other constituents of the mixture could easily be undergoing a similar or more complex mass transfer, the movement of each specie under pure molecular diffusion is controlled by local concentration gradients. Observation of this dependency has led to a formulation of a quantitative description of diffusion in the form of Fick's law, which states:

$$\begin{bmatrix}\text{Mass flux}\\ \text{Specie A}\end{bmatrix} = \begin{bmatrix}\text{Proportionality}\\ \text{term}\end{bmatrix} \times \begin{bmatrix}\text{Local con-}\\ \text{centration}\\ \text{gradient}\end{bmatrix} + \begin{bmatrix}\text{Flux caused}\\ \text{by bulk flow}\\ \text{of mixture}\end{bmatrix}$$

The proportionality term between the mass flux and the concentration gradient is the diffusivity, and it is a physical property analogous to other transport properties such as viscosity and thermal conductivity. Thus, at some point in a system an instantaneous rate of diffusion can be described as a function of system physical properties and the concentration gradient. This diffusion induced flow can then be added to the bulk flow of the mixture resulting from such body forces as pressure and gravity for a complete flow description. It is from this relationship that mathematical models for mass transfer in turbulent flow systems, in gas absorption operations, product flow through heterogenous catalyst beds, etc. can be developed.

In a gaseous systems at normal ambient temperature and pressures diffusivity is normally considered a constant and both theoretical predictions and experimental results tend to confirm this situation. Whereas a constant diffusivity for gas systems at these mild conditions is truly representative within a normal error of perhaps only a few percent, it is both expected and experimentally verified that diffusivity becomes markedly a function of composition as conditions approach those of a condensed gas.

Attaching a numerical value to the diffusivity for some binary gas system currently is approached through theoretical correlations or through experimental work. The theoretically determined values are correlations derived from gas kinetic models of varying

complexity, but any reasonably general correlation does not always predict the actual diffusivity precisely. For this reason experimentally obtained diffusivities have value, not only for their calculational value, but as data for comparing theoretical correlations.

Of course, experimental methods of data acquisition are frequently tedious and of restricted versatility. Measurements of binary gas phase diffusivity are not exceptions. Currently, experimental determinations of diffusivity are based upon observations of controlled diffusion taking place in specially designed diffusion cells. From assumptions as to the behavior of the particular systems under study and by application of various detecting devices, the results can be analyzed for diffusivity. Because of the experimental difficulty in measuring a concentration gradient at a specific point or gas composition the analysis is normally accomplished by mathematical integration or some other averaging of the concentration gradient. This inevitably leads to results or a diffusivity representing an average over a range of composition.

In view of this situation surrounding experimental measurements of gas phase diffusivity, a method which produces accurate values at a given point value of system composition over a wide range of conditions and compositions is of definite value. Pursuit of such an experimental method is the scope of this project.

BACKGROUND AND SCOPE

Previous Work

Two classical devices for determining gas phase diffusivity are the Arnold[1] cell and the Loschmidt cell. Arnold cell methods which allow a solvent vapor to diffuse at steady state are very straightforward experimental methods yielding precise results without complex apparatus (Lee and Wilke, 1954; Godfrey, 1969). On the other hand, a Loschmidt cell (Boyd et al., 1951; Berry and Koeller, 1960) can be applied to superheated gaseous mixtures, but requires a composition sensing apparatus. Unfortunately, uncomplicated analysis of the results of experiments using Arnold and Loschmidt cells requires that the diffusivity be assumed to be a constant at a given temperature and pressure; i.e., not a function of composition.

Because both Arnold cells and Loschmidt cells have limitations in their normal mode of operation, a number of other techniques have been used and reported in the literature. A method described by Hu and Kobayashi (1970) for measuring gas phase diffusivity in the region of tens of atmospheres is noteworthy for the particular attention to work with dilute systems to eliminate composition effects. Of particular interest is the work reported by Woessner et al. (1969). That

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[1] Also referred to as a Stefan cell. The term Arnold cell is used throughout this text.

experimental work was carried out with light alkanes well into the dense gas region and concentration gradients were detected by NMR spin echo techniques. They reported the measured binary diffusivity as varying with composition by a factor of two to three. Of course, their apparatus is both costly and requires skilled experimenters.

That diffusivity of a binary gas system is composition dependent has been noted previously and was the subject of experimental work carried out by Prabhu (1966). He investigated the chloroform-air system and the methanol-air system at pressures of about one atmosphere and temperatures of 50° and 55°C, finding a negligible composition effect for methanol-air, but a definite variation of chloroform-air diffusivity with composition. From these results he showed that an average value of diffusivity for chloroform-air over a range of composition varied[2] from 0.106 cm^2/sec to 0.115 cm^2/sec. Although these diffusivities were obtained by using an Arnold cell, it had to be operated in a mode of varied boundary conditions which magnified the amount of data required, and the numbers represented average values over given composition ranges, not values at a specific mole fraction of chloroform. In another experiment a slight tendency for lowering of diffusivity with increasing ethane concentration was noted in a Loschmidt cell with an ethane-hydrogen system, but the results

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[2] The higher value was for a chloroform mole fraction range of 0.682 to 0.566 while the lower value applied to a range of 0.682 to 0.

were again averages over small composition ranges (Boyd et al., 1951).

In addition to such experimental methods some theoretical approaches to estimating binary gas system diffusivity have been developed. These approaches have been marked by a trend to develop more realistic kinetic models which truly represent binary molecular interactions (Sharkey, 1968). Still, the molecular force fields assumed in order to carry out the calculations suggested by these models are constrained to simplicity and diffusivities so calculated can only predict observed values with errors of five percent or greater (Chen and Othmer, 1962). Some of the most common correlations for gas phase diffusivity (Bird et al., 1960) are based upon rigid sphere molecular models and have no allowance for composition corrections. Consequently, the current situation is that both theoretical correlations and experimental techniques for obtaining numerical values usually do not allow for composition effects. Those experimental methods that do take into account variation of diffusivity with composition are either quite limited or laborious. In light of this situation, it appears that a straightforward means of experimentally measuring composition profiles in a basically simple Arnold cell would be an ideal way to determine diffusivity at specific point values of composition.

Of the numerous properties of a binary mixture of gases which

can be sensed and measured to determine composition, optical refractive index is exceptionally well suited to diffusivity measurements. The advantages are the high precision of simple detection devices and the non-disturbance of the gas by sampling. Detection of composition changes through refractive index variation using interferometers has been previously applied to diffusivity measurements by Boyd et al. (1951) and Sharkey (1968).

A wide variety of interferometers which can detect minute changes in refractive index have been described and constructed which could be applied to diffusing gas systems. Bryngdahl and Ljungren (1960) have described and analyzed a Savart plate interferometer using plane polarized light, and although it has been used successfully with liquid systems, it involves costly optical components. Some of the most common types of interferometers such as the Michelson, Mach-Zender, and Fizeau have been analyzed in great detail in classical treatises on physical optics (Ditchburn, 1963) and their behavior is well understood. If the composition-refractive index relationship of a binary gas system can be precisely established, then one of these common devices would offer a simple and economical approach to measuring gas phase composition gradients in a diffusion cell. Discussions of such relationships for gases have been summarized by Partington (1953), and fortunately a simple linear relationship between mole fraction and refractive index of a binary system is very accurate.

Obviously there would be considerable benefit to applying an optical interferometer to detect refractive index changes and hence composition variation in an Arnold cell. The Arnold cell diffusion process is well understood and if the composition profile can be accurately measured, the concentration gradient and ultimately diffusivity can be evaluated at any specific composition value. Accomplishment of this task was defined as the objective of this project.

Project Scope

The specific scope of this project was to develop an optical method of measuring the gas phase concentration profiles in an Arnold cell in order to precisely establish the diffusivity variations with composition observed by Prabhu (1966). Thus the first objective was to design a system using an optical interferometer with an Arnold cell which could simulate the experimental conditions encountered by Prabhu (1966). Then the experimental apparatus was to be constructed in accordance with this design and experimental techniques developed. Lastly, the precision of this experimental approach was to be analyzed to determine its suitability for precise diffusivity measurements.

Criteria for attainment of these objectives were devised in order to define the points of completion and provide a measure of progress. The criteria established were:

1. Composition profiles reproducibly measured within experimental accuracy would verify the design approach.
2. Accurate determination of concentration gradients from these profiles in order to calculate diffusivity with enough precision to detect composition effects of the magnitude predicted from Prabhu's (1966) results would establish the validity of this experimental technique.
3. Close agreement between the results of this experimental work and previous work would confirm the validity of the numerical results.

QUANTITATIVE RELATIONSHIPS

Diffusion in an Arnold Cell

Accomplishing the objectives defined for this project required that the diffusional and optical phenomenon dealt with be thoroughly and quantitatively described through a series of mathematical equations. Only in this manner could a proper and reliable system design be attained and a proper analysis of the experimental results be later carried out.

Diffusion behavior of an Arnold cell is easily described by a differential equation as developed in detail by Bird et al. (1960). With the symbols and terminology used in this discussion the equation takes the form:

$$\overline{N}_A = -C \mathcal{D}_{AB} \overline{\nabla} y_A + y_A(\overline{N}_A + \overline{N}_B) \qquad (1)$$

The mass fluxes, $\overline{N}_i$, and composition gradient, $\overline{\nabla} y_A$, are vector quantities which are limited by the Arnold cell configuration to have only an axial component. In addition, the physical conditions of time, temperature, pressure, and the nature of the chemical components of this project justify the assumptions listed in Table 1.

When these assumptions are applied to equation (1) in an Arnold cell with geometrical relations as shown in Figure 1, the following equation (2) describes diffusion in an Arnold cell.

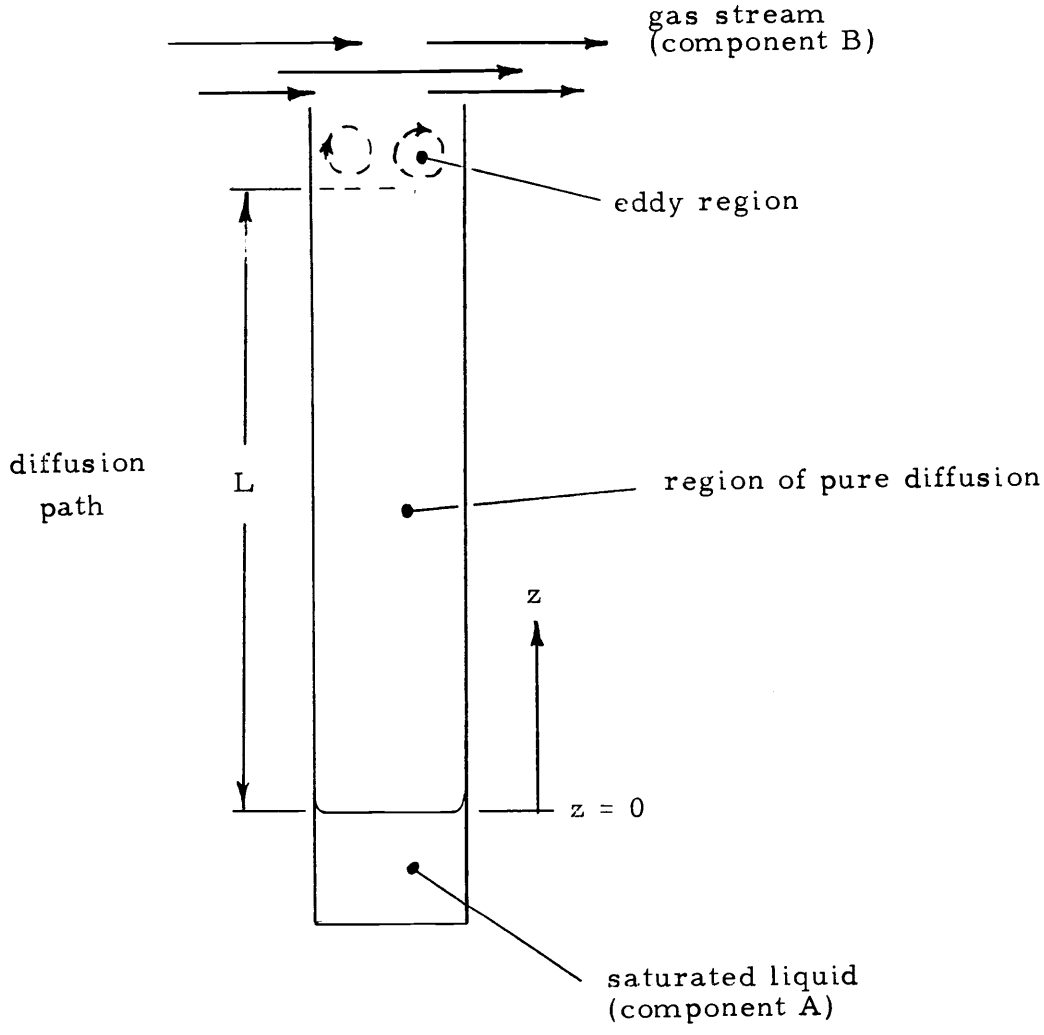

Figure 1. Arnold cell schematic representation.

Table 1. Assumptions for Arnold cells.

1.	Component B is insoluble in liquid A and has no net mass flux.
2.	Cross sectional area of cell is constant.
3.	Diffusion is occurring at steady state.
4.	Molar density is described by ideal gas law.
5.	No chemical reactions occur.
6.	Mass flux of component A is constant throughout length of cell.

$$\frac{\Delta W_A}{M_A A_{xx} \Delta t} = -\left(\frac{P \mathcal{D}_{AB}}{RT}\right) \frac{\left(\frac{dy_A}{dz}\right)}{1-y_A} \tag{2}$$

If the experimental conditions of temperature and pressure are maintained with sufficient accuracy, then diffusivity might be determined in two manners. A sufficient flow of gas B across the cell top will maintain the mole fraction of solvent vapor, component A, at zero at that position. Also the system pressure and vapor pressure of component A will determine the equilibrium composition of A, y_{eq}, at the liquid interface. If diffusivity is considered a constant, then equation (2) can be treated as a boundary value problem, integrated, and then solved for diffusivity with the form of equation (3).

$$\mathcal{D}_{AB} = \frac{\Delta W R T}{L M_A P A_{xx} \Delta t \ln\left(\frac{1}{1-y_{eq}}\right)} \tag{3}$$

This is the normal experimental approach in Arnold cell work

where all terms on the right hand side of equation (3) are measured experimentally. However, if an unknown diffusivity is not a constant, then the integration leading to equation (3) cannot normally be carried out and some approach such as that used by Prabhu (1966) would have to be substituted. When the composition profile of component A in the Arnold cell can be experimentally measured with sufficient precision to evaluate the derivative, dy/dz, then diffusivity can be determined in another manner. The terms in equation (2) can be experimentally evaluated and the diffusivity expressed as in equation (4).

$$\mathcal{D}_{AB} = - \frac{\Delta W \; R \; T \; (1-y_A)}{M_A P \; Axx \; \Delta t (\frac{dy}{dz})} \tag{4}$$

The only assumptions applicable in this equation are those listed in Table 1 and diffusivity is not constrained to be a constant. The key point is that the composition profile must be determined with a high degree of accuracy. That this is feasible is shown by considering the principles of physical optics.

Physical Optics Fundamentals

Because light is an electromagnetic phenomenon it can be described by Maxwell's equation for the electric vector:

$$\nabla^2 \overline{E} = (\epsilon \mu) \frac{\partial^2 \overline{E}}{\partial t^2} \tag{5}$$

The solution to this equation is the equation of a monochromatic light wave propogating with velocity $1/\sqrt{\epsilon\mu}$. Born and Wolf (1965) state that at normal conditions of dielectric gases, even into the moderately dense region, the permeability, μ, is essentially that of free space and the permittivity, ϵ, is dependent upon intramolecular properties. Thus, with the gases commonly experimented with in Arnold cells, the velocity of propogation of a light beam is related to the refractive index, n, as in equation (6).

$$v = \frac{1}{\sqrt{k}\ \sqrt{\epsilon_0\ \mu_0}} = \frac{c}{\sqrt{k}} = \frac{c}{n} \tag{6}$$

Continuity of the electric field at any dielectric boundary requires the frequency, ν, to be constant and this allows the wavelengths in a gas space to be related to geometry and intramolecular properties of the gas (refractive index) as:

$$Q = \frac{X\ \nu\ n}{c} \tag{7}$$

For sodium D light, c is a universal constant of value 3.00×10^{9} cm/sec, and ν is 5.09×10^{14} cycles/sec.

Following the recommendations of Weinberg (1963) the gas mixture refractive index is represented as a linear function of molar composition.

$$n = y_A n_A + y_B n_B \tag{8}$$

This is a very simple relationship, but at the conditions encountered experimentally in this project, it introduces errors less than detectable with the apparatus available.

These relationships can be combined with constraints of constant temperature, pressure, and geometry to correlate the number of wavelengths, Q, to the gas mixture composition in the Arnold cell as equation (9).

$$Q = \frac{s\nu}{c}\left[n_B + y_A (n_A - n_B) \right] \tag{9}$$

Differentiation of this equation yields a linear relationship which can be interpreted as relating an integral change in number of wavelengths in the cell to a small change in composition (equation 10).

$$\frac{1}{\frac{dQ}{dy}} = \frac{c}{s\nu\ (n_A - n_B)} = \frac{\Delta y}{\Delta Q} \quad \frac{\text{mole fraction}}{\text{wavelength change}} \tag{10}$$

When the constant experimental parameters of cell geometry and type of light source used in this project are evaluated and inserted into equation (10) for c, s, and ν, the relationship becomes:

$$\frac{1}{\Delta Q} = \frac{4.195 \times 10^{-6}}{(n_A - n_B)} \quad \frac{\text{mole fraction}}{\text{wavelength change}} \tag{11}$$

Detection of wavelength shifts of a light beam by means of an interferometer is dependent upon the superposition of phase shifted spatially coherent light. A simplified illustration of an interferometer is shown in Figure 2 and detailed development of functional characteristics of these devices can be found in Ditchburn (1963). Through any

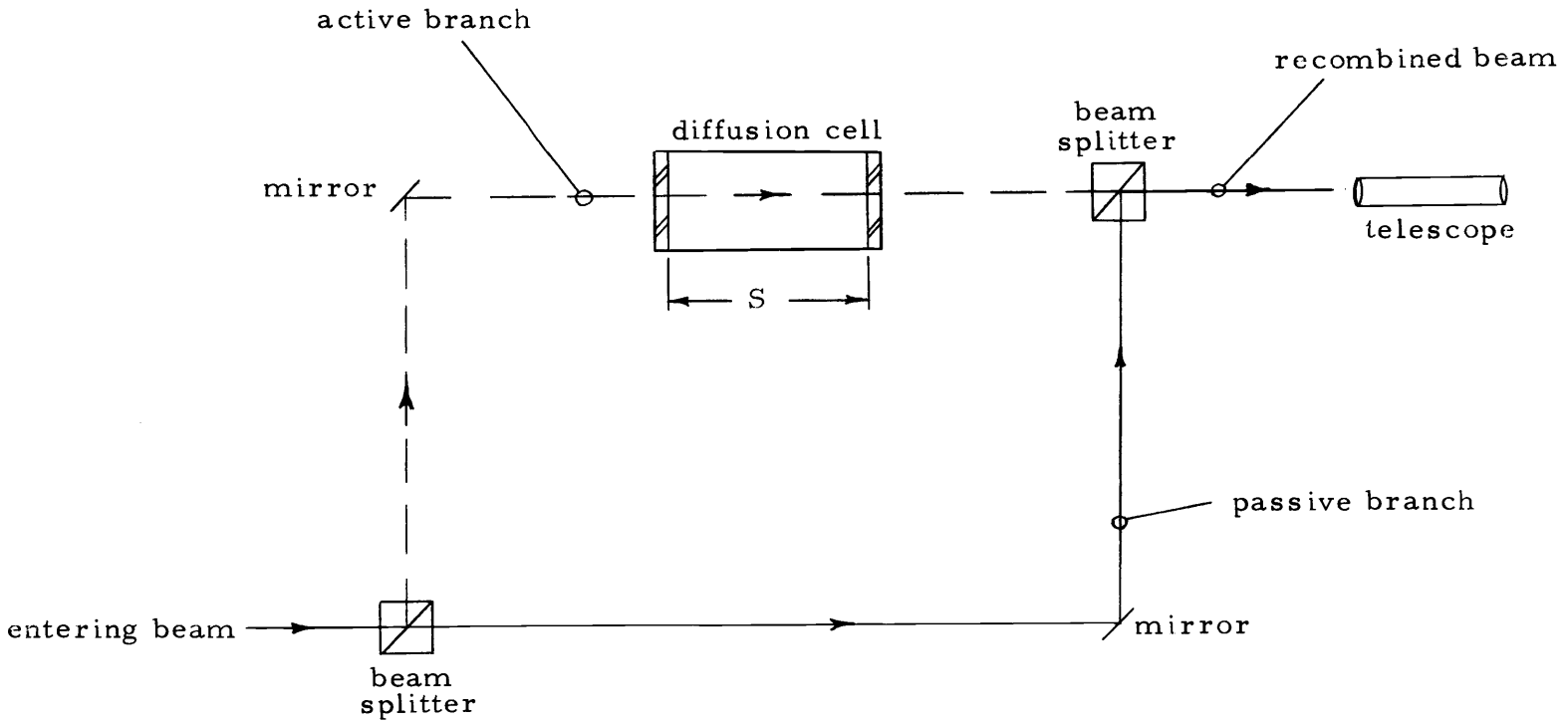

Figure 2. Schematic representation of Mach-Zender interferometer.

segment of such an interferometer the number of wavelengths can be determined by equation (7). So long as the passive branch configuration and medium refractive index is constant, the wavelengths in this branch will be constant in number and will serve as a reference for the active branch. Similarly for the active branch, if the only change in the optical path occurs in the cell and the external portions maintain constant length and refractive index, then the recombined beam's amplitude can be expressed by superposition.

$$E = (E_{act})e^{2\pi i(\nu t - Q_{act})} + (E_{pass})e^{2\pi i(\nu t - Q_{pass})} \tag{12}$$

This equation can be modified to obtain a closer comparison of the two branches by expressing the active branch number of wavelengths as:

$$Q_{act} = Q_{pass} + (Q_{act_0} - Q_{pass}) + \Delta Q \tag{13}$$

Than at some selected location in the beam $(Q_{act_0} - Q_{pass})$ will be an integral number due to the very short wavelength of light, and $e^{2\pi i(Q_{act_0} - Q_{pass})}$ will be equal to 1.0. Then equation (12) can be rearranged using these relationships to the form:

$$E = e^{2\pi i(\nu t - Q_{pass})}[E_{pass} + E_{act}\, e^{-2\pi i\, \Delta Q}] \tag{14}$$

The implication of equation (14) is that as ΔQ changes continuously due to a change in refractive index in the Arnold cell, the resultant amplitude of the recombined beam will progress from a maxima, through a minima, and back to a maxima. Thus an

observation of one fringe shift by an interferometer such as shown in Figure 2 caused by moving the interferometer a measured distance along a concentration gradient is directly related to a composition change given by equation (10). By noting the position of each successive fringe shift when the interferometer traverses the Arnold cell from a known starting point, a precise concentration profile can be developed. With that information the terms (1-y(z)) and d/dz(y(z)) in equation (3) can be determined and if the mass flux value, N_A, can be computed by the time and weight change measurements in the manner indicated by equation (4), then the gas phase diffusivity $\mathcal{D}_{AB}$ can be calculated at any and all values of y_A present within the cell.

APPARATUS

General Description

Pursuing the objective of this project, an apparatus was constructed to measure composition gradients at various points in an operating Arnold cell. The core of the experimental system was a modified form of an Arnold cell, and was supplemented by other units to provide control of experimental physical parameters and assure steady state conditions.

Composing the diffusion cell subsystem were the Arnold cell, wherein the gas phase diffusion occurred, a temperature control unit, a unit to replenish evaporated liquid solvent and a unit to flow gas across the cell top. The units in the optical subsystem were the interferometer which detected concentration changes, a monochromatic light source, a light collimating unit, and the framework which held and positioned the interferometer. When combined, these two subsystems were used to obtain the experimental measurements of mass flux and composition profiles.

Diffusion Cell Subsystem

Arnold Cell Unit

The actual Arnold diffusion cell in relation to other diffusion cell subsystem units is shown in Figure 3, and the details of the cell are

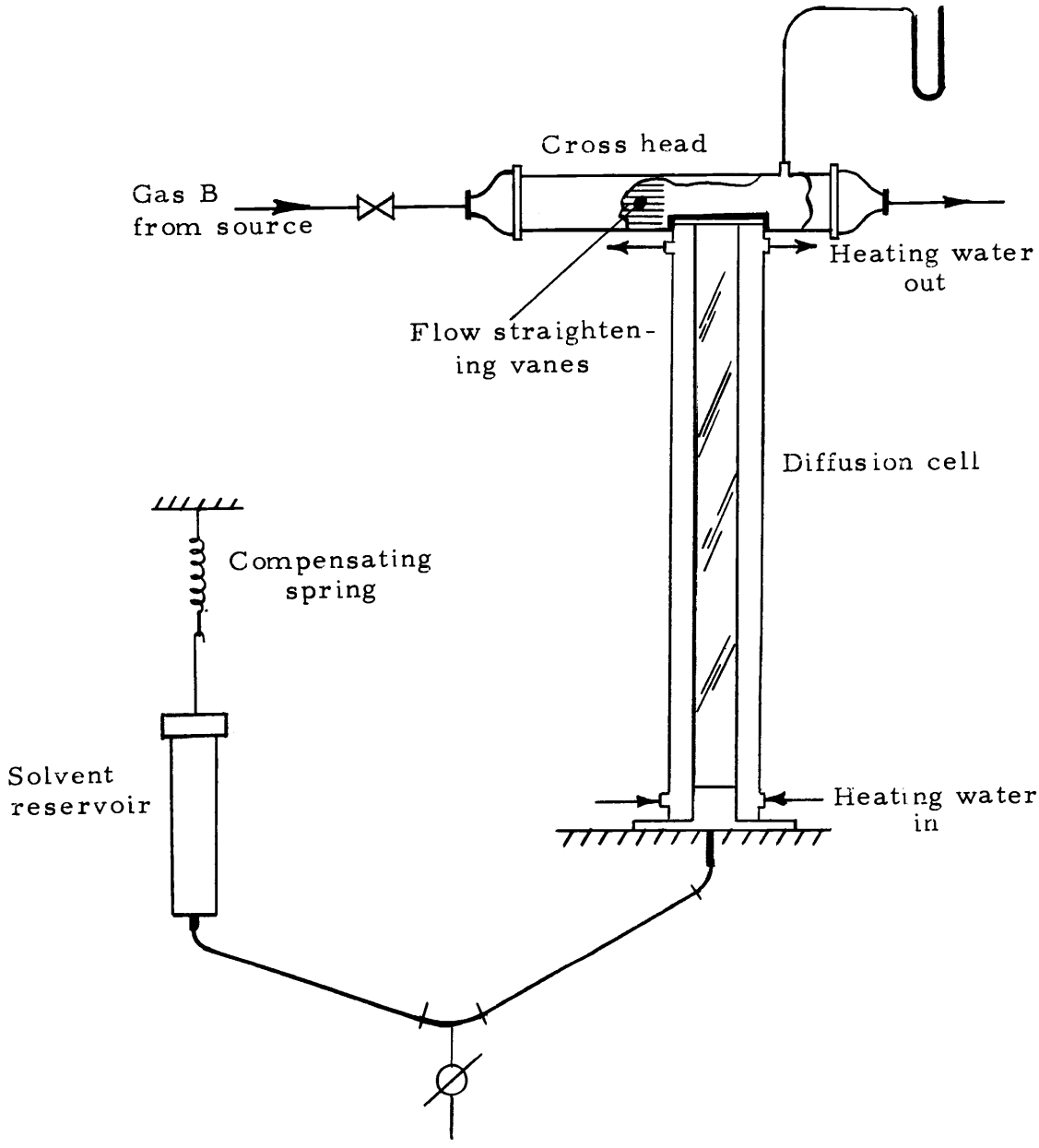

Figure 3. Representation of integrated diffusion cell subsystem.

shown in Figure 4. The cell interior cross section was uniformly rectangular with an area of 4.92 cm^2, and the overall interior length was 31.2 cm. The transparent material for both front and rear sections was commercial quality 1/4 inch (0.635 cm) thick plate glass. The other two side walls were portions of aluminum channels which allowed integral heating of the cell. This cell configuration was a compromise between ease of fabrication and procurement, providing a reasonable optical path for high sensitivity, and providing a reliable means of cell temperature control.

By constructing the Arnold cell with hollow channels for sides, its geometry could be kept compact for easy integration with the optical interferometer, yet be capable of maintaining selected isothermal conditions. These hollow rectangular channels were 1100 alloy aluminum extrusions with walls 0.318 cm thick. Machined aluminum blocks were bonded with an epoxy-polyamide adhesive to the channel ends to form a base and an end cap. At the base of the Arnold cell was a shallow well to hold liquid solvent for evaporation and diffusion upward through the stagnant gas column. This well consisted of a soldered 0.076 mm gage brass foil insert, 1.0 cm deep, and fitting snugly against the cell base and walls.

In order to minimize optical distortion, the glass strips were mounted in a manner which allowed them to be aligned parallel and to remain separated a constant length regardless of cell temperature

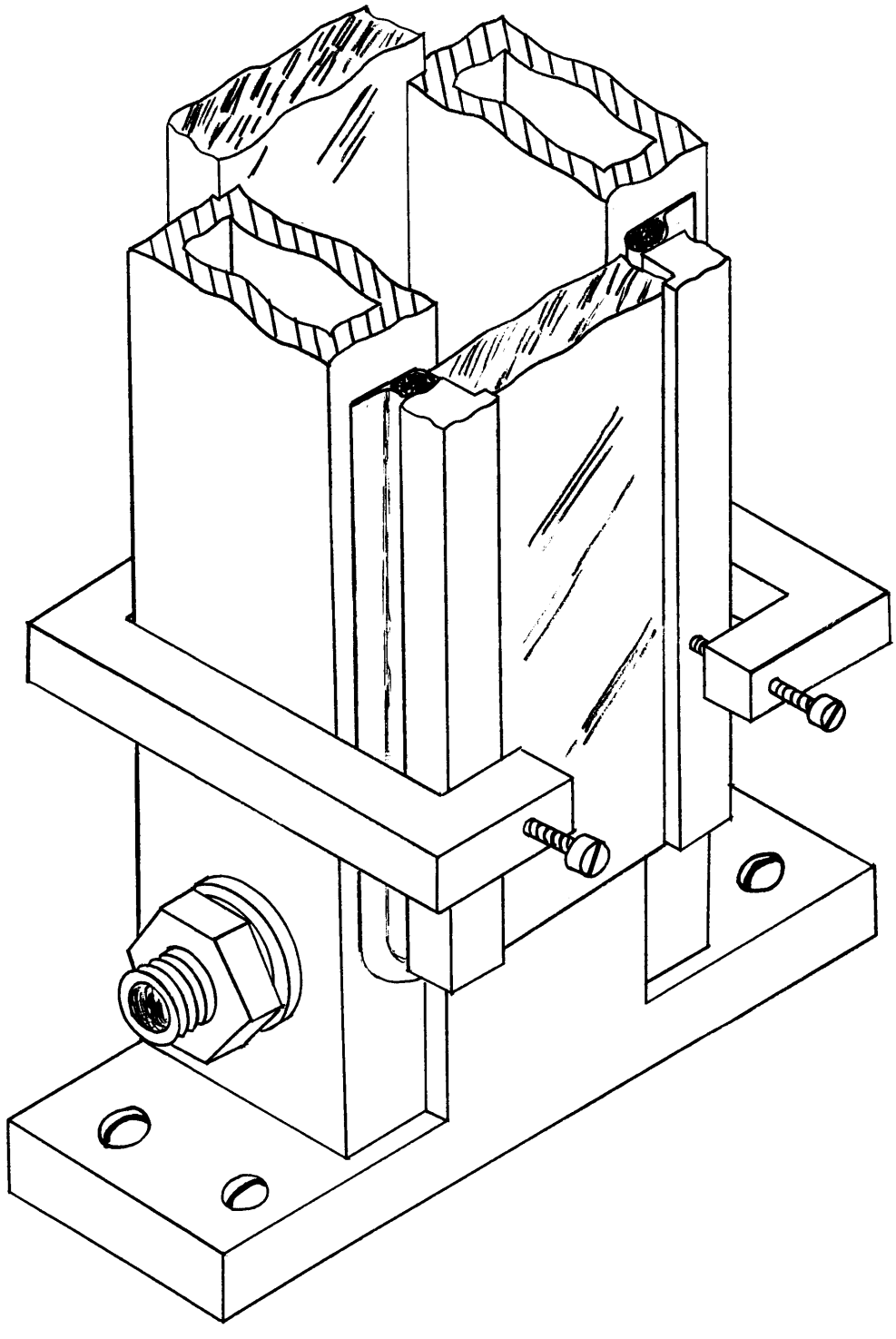

Figure 4. Detailed configuration of diffusion cell (scale 1-1/2 to 1).

changes. The back glass strip was bonded to the aluminum channels as shown in Figure 4 and the front glass strip was held in place by three pairs of 36 nickel low expansion alloy (Invar) clamps. A special gasket was employed to seal the front glass, and the aligned glass sides were subsequently filleted with single component RTV silicone sealant to enhance heat conduction to the glass from the aluminum walls.

Temperature Control Unit

An apparatus for controlling the cell's temperature was separate from the Arnold cell. In simplest terms this unit consisted of a tank of heated water, a pump which recirculated this water from the tank through the inside of the cell channel walls back to the tank, and a temperature controller.

Temperature control was accomplished with an electronic controller operating in the proportional mode[3] and regulating power to a 250 watt immersion knife heater. The centrifugal pump discharge was split through a tee for approximately equal flow through each cell channel. The discharge from the upper ports on the cell channels then emptied directly into the tank. Through the action of this temperature control unit a diffusion cell temperature could be selected

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[3]Thermotrol Model 1035, manufactured by Hallikainen Instruments, Richmond, California 94804.

and maintained with less than $\pm$ 0.4°C fluctuation.

Solvent Delivery to Diffusion Cell

Two separate methods were used to supply liquid solvent to the Arnold cell as a source of the diffusing component of the binary gas systems studied. When making measurements of composition profiles the solvent delivery unit was employed, and when making mass flux measurements a special insert cup holding a small amount of solvent was used.

Figure 3 shows the basic operation of the solvent delivery unit. An aluminum tubular reservoir, counterbalanced and suspended from a compensating spring, held the bulk of the liquid. From the bottom of this reservoir the solvent flowed through a Teflon TFE plastic tube, through a drain stopcock, and into the cell-well insert bottom. Springs of varying stiffness were used with different solvents, depending upon the solvent liquid density. With this arrangement a steady level of solvent was maintained in the cell for the duration of an experimental run.

Unfortunately, it was found that the polymeric materials used in the solvent delivery unit tubing and joint seals leaked. This leak rate was small, but of the same magnitude as the mass flux evaporation rates in the Arnold cell. This situation prevented a simple weighing procedure for solvent charged and solvent recovered from

this unit to be used in determining mass flux due to diffusion. For this reason a small brass insert cup was constructed to obtain mass flux data. This cup could be filled with solvent, suspended at various positions in the cell, and later removed and the weight change measured.

Cross Head Gas Flow Unit

In addition to the solvent vapor source from the liquid in the Arnold cell-well, a continuous flow of the non-diffusing gas across the cell top was required. A unit to provide a metered and laminar flow of this second component of the gas systems studied was constructed. As shown in Figure 5 the gas was supplied from a compressed gas bottle in the case of nitrogen, or from the building compressed air lines. From the gas source the gas flowed through a dessicant filled drying tube, through a Brooks model 2-15-3 rotameter for flow rate measurement, then through a coil of copper tubing immersed in the heated water tank, and then through the cross head.

The cross head device was constructed from a length of standard pipe of 2.66 cm ID with reducing end fittings. This center pipe section of the cross head was 18 cm long and contained a bank of horizontal straightening vanes immediately ahead of the cell opening. Mating of the cross head to the cell, as shown in Figure 4, was through a rectangular machined opening in the pipe bottom. The exit end of

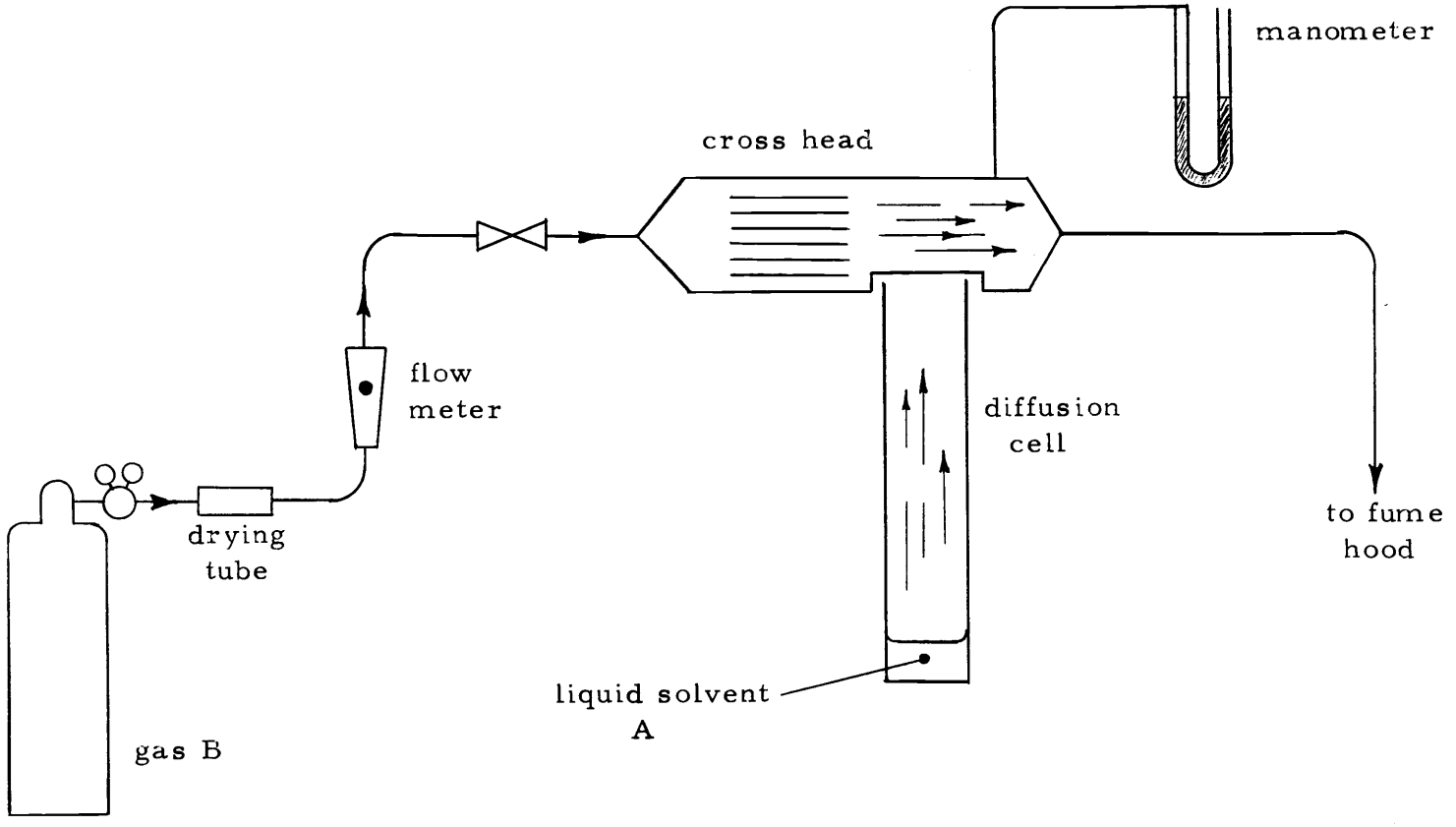

Figure 5. Schematic flow diagram of gaseous components.

the cross head was constructed of small diameter pipe in such a manner that the entire cross head could be swung upward on its mounting brackets away from the Arnold cell. A length of polyethylene tubing several meters in length carried the gas and vapors leaving the cross head to a fume hood where they were discharged from the system.

By means of this unit a steady flow of the second component, the non-diffusing one, of the gaseous systems was directed across the top of the Arnold diffusion cell. This flow could be regulated to effectively sweep away all solvent vapor which diffused to the cell top and thus assure the mole fraction of the diffusing component was kept at zero at the cell top.

Optical Subsystem

In addition to the diffusion cell subsystem just described, an optical subsystem designed to measure the composition profiles developed in the Arnold cell was constructed. The basic unit in the optical subsystem was a Mach-Zender type of interferometer which produced an interference fringe pattern like that of a Michelson interferometer. In addition, units to produce a monochromatic light beam, a viewing telescope, and a supporting and positioning framework were designed and constructed.

Interferometer Unit

The behavior of an interferometer with one of the split beams passing through a gas filled cell has been described earlier in the section on quantitative relationships. The interferometer design for this project employed a narrow beam of rectilinear light directed through the cell six times in a horizontal zig-zag pattern. This "slice" of the cell would contain gas of approximately uniform refractive index and the interference ring fringes would be only slightly distorted. Then the whole interferometer was designed to move vertically as a single unit so that gas of varying composition and refractive index would pass across the active beam as it moved in the direction of a composition gradient.

A top view of the interferometer unit showing the lay-out of the optical components and path of the active branch beam through the cell is shown in Figure 6. Light projected upward from the collimator was brought horizontally onto the interferometer platform by a canted mirror (M_{10}). From the first beam splitting prism (P_1) to the second recombining prism (P_2) the light was split into two branches, one active and one passive. The passive branch composed of mirrors M_6 through M_9 was assumed to consist of a constant number of wavelengths as given by equation (7), and served as the reference to which phase shifts caused in the active branch could be detected by expansion or contraction of the interference pattern.

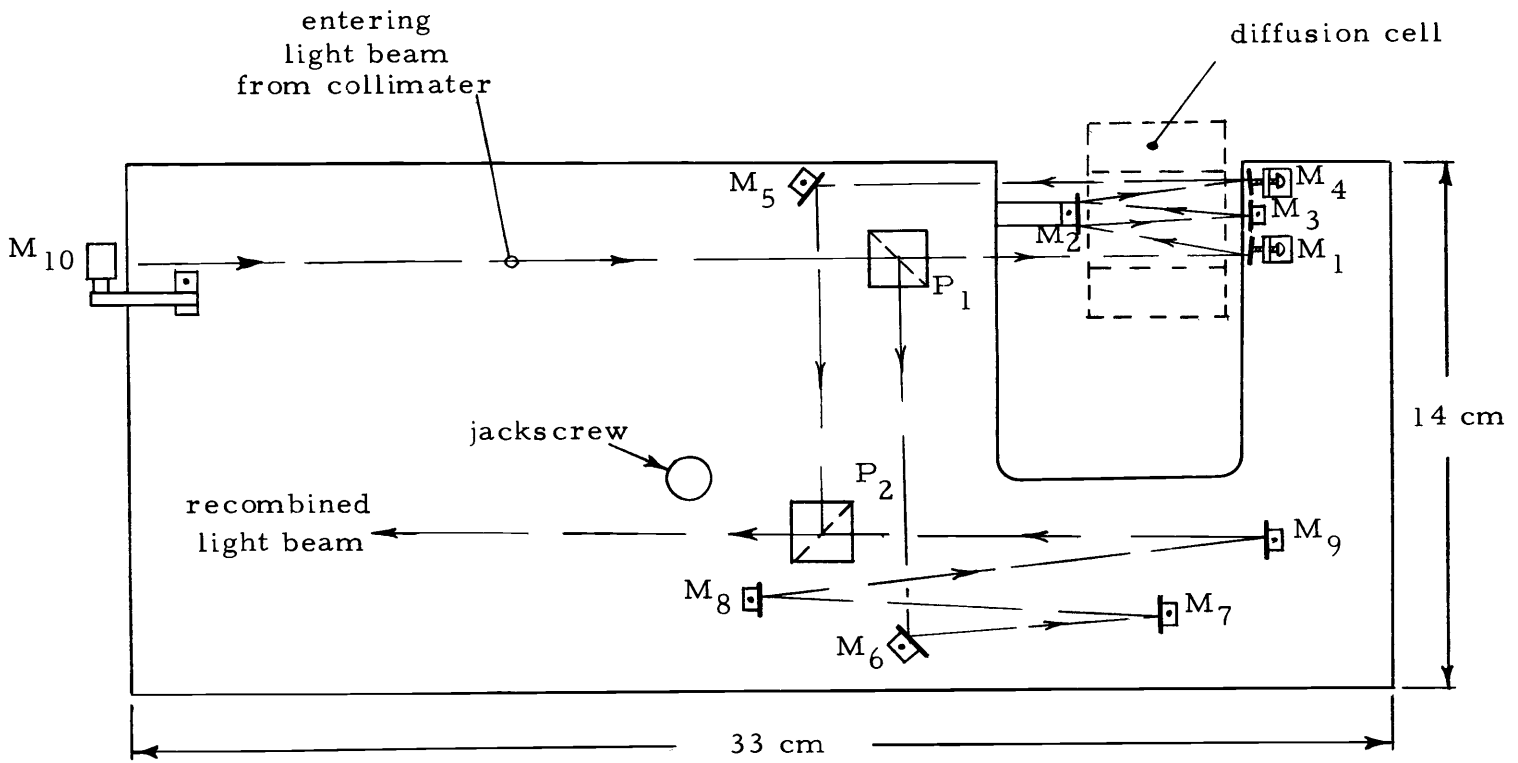

Figure 6. Layout of optical interferometer platform (scale 1/2 to 1).

The base plate on which the components were mounted was a 0.65 cm thick plate of annealed 36 nickel low expansion alloy (Invar). Use of this material eliminated need for temperature compensation of experimental fringe patterns taken at different ambient conditions. All optical components were rigidly mounted on this plate with adjustments for elevation accomplished with metal shims. Each of the beam splitting prisms was a cube 15 mm on a side with a partially silvered diagonal plane. The mirrors were front surface types, approximately 9 mm square. Of particular note should be the fact that these components were only common scientific quality, not of the precision quality commonly associated with interferometer devices.

Also attached to the interferometer unit were guide rail pads and cell glass wall insulation strips. The guide pads were attached to rigid brackets which extended out and around the twin vertical guide rails of the framework. The pads themselves were machined from Teflon TFE and served to fix the horizontal position of the interferometer and still allow smooth vertical movement. Polystyrene foam insulation strips were also attached to cover the cell glass sides in all areas except where the active branch beam passed through the Arnold cell.

Supporting Framework

Because the optical subsystem design embodied the concept of a

movable interferometer, a special jackscrew and guide rail framework were constructed. A pair of 8 rms finish smooth ground class 304 stainless steel bars bolted parallel to a welded steel frame served as the vertical interferometer guide rails. Actual support of the interferometer was accomplished by a jackscrew and a nut bolted to the interferometer unit platform. The jackscrew was 58 cm long and 1.27 cm diameter (1/2 - 20 NF). A hand crank was attached to the upper end of the jackscrew, and when the screw was turned, the interferometer would ride along the guide rails and vertically traverse the diffusion cell.

Light Source and Collimator

Direction of a monochromatic light beam into the interferometer from an arc lamp is illustrated in Figure 7. The light source was a bright 85 watt sodium vapor arc lamp.[4] This lamp was positioned to direct light from the bulb into the collimating unit condenser lenses.

All elements of the collimating unit were mounted on a wooden base which allowed flexibility in positioning. The condenser lenses focused the lamp on a pinhole screen, thereby producing a monochromatic point source of light shining into the collimating lens. The collimating lens was mounted in a 24 cm long barrel which was in turn

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[4] George W. Gates and Co. Model SLA-5C power supply and housing with a General Electric Na-1 bulb.

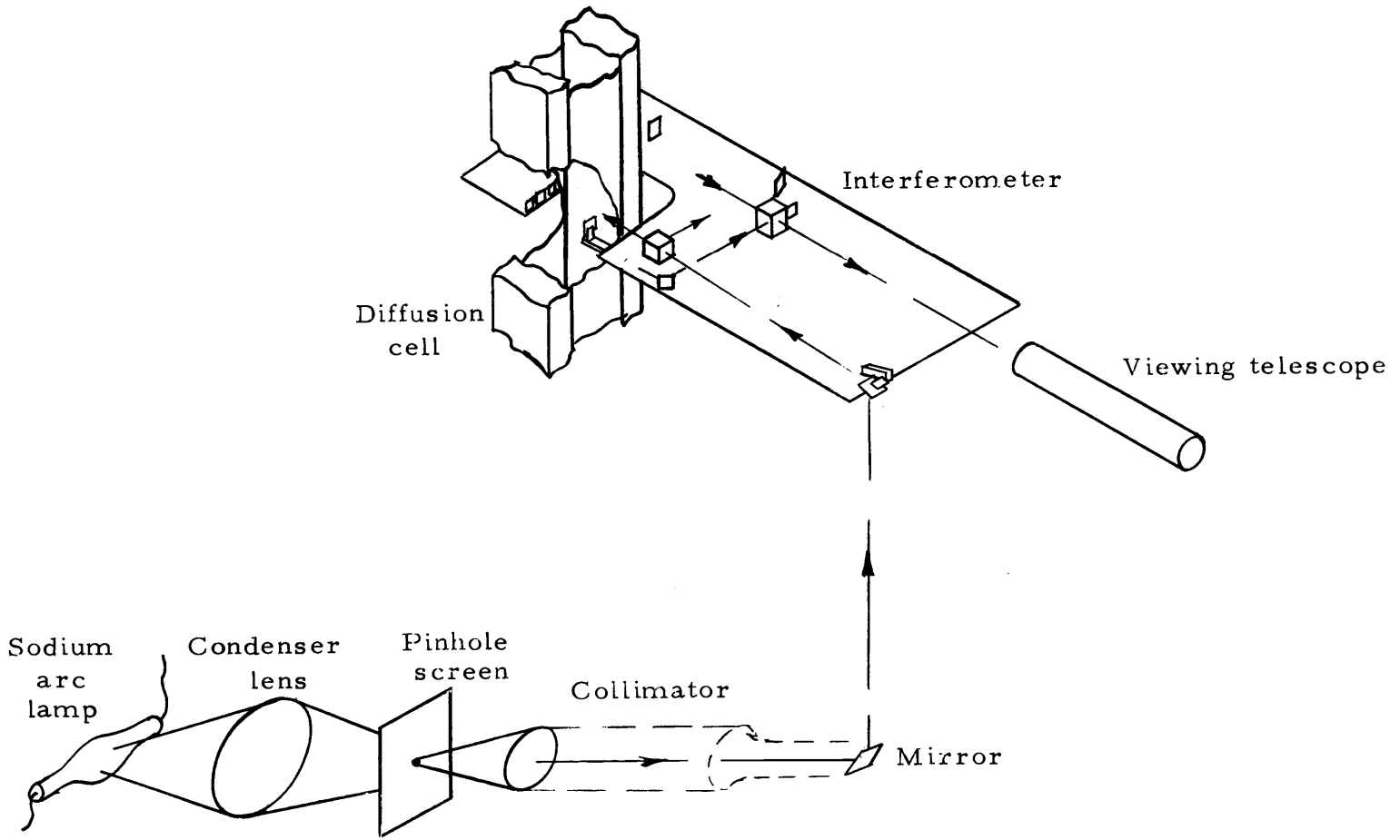

Figure 7. Layout of integrated optical subsystem.

mounted with adjustable screws to the collimator base. This arrangement allowed the collimator barrel to have adjustment capability in both azimuth and elevation. At the opposite end of the collimating barrel a front surface mirror was placed at a 45^{o} angle in order to direct the collimated light beam upward precisely along the direction of travel of the interferometer.

No light filters were used in this subsystem since the arc lamp produced a very bright yellow light characteristic of the sodium spectrum. Because of this bright source and the non-precision quality optical components used, the need for filters was not justified and the yellowish interference pattern observed was assumed to be due solely to the sodium D line of the spectrum. This pattern of fringes produced by the integrated lamp, collimator, and interferometer units was easily viewed with the viewing telescope.

Viewing Telescope

Although the interference fringe pattern produced by the optical subsystem could be seen with the naked eye, a terrestrial telescope was employed to view a magnified portion of the fringe pattern. The telescope itself was one normally used on a surveying transit with an internal cross hair. This telescope was mounted on a special counterweighted bracket attached to the interferometer supporting framework. The attachment was made in such a manner that the support was made

through pads against the guide rails and a pair of nuts running on the jackscrew. Through this arrangement the telescope was positioned with its axis along the recombined exiting beam as shown in Figure 7 and would precisely follow the interferometer movement. When focused on infinity a broad interference pattern could be seen and movement of minima and maxima past the cross hair could be easily observed. With this total integrated optical subsystem, the interference pattern could be continuously viewed as the diffusion cell was traversed vertically. If the cell contained a gas mixture of varying composition, and hence refractive index, a continuous expansion or collapsing of interference fringes could be seen and each fringe shift counted.

Instrumentation Subsystem

Since measurement of a varying concentration profile required simultaneous detection of both composition and position, a special instrumentation subsystem was assembled. By means of a target fixed to the interferometer unit and a cathetometer, the position of the interferometer with respect to the diffusion cell could be determined. By means of a digital shaft encoder the number of jackscrew turns and thus interferometer movement away from some known position could be determined. The output from this shaft encoder was inputed to one channel of a dual channel variable speed paper chart

recorder. Thus, starting at some known position, net movement away from that position was automatically recorded on the chart recorder output.

Although the detection of a fringe shift was visual, a hand held counter was employed to record each net shift. Starting from a known position of the interferometer the jackscrew shaft encoder would record subsequent positions while the hand counter would mark fringe shifts through the other channel of the chart recorder. With this arrangement the concentration profile could be calculated from the output data.

Other required operating parameter data were determined from auxiliary instruments. Elapsed times could be determined from simple clock readings, and cell pressure could be determined from a mercury barometer and cross head manometer. Weights of liquid solvent were measured on an Ohaus triple beam balance sensitive to 0.01 gram. Temperatures of liquid and vapor in the cell were measured with an iron-constantan thermocouple and potentiometer capable of being read to $\pm$ 0.001 mv. The thermocouple wire was inserted through a length of small diameter glass tubing which allowed the thermocouple bead to be positioned at various points within the Arnold cell.

When all units of the experimental system were integrated it was possible to create the conditions and obtain measurements on an

operating Arnold diffusion cell. Mass fluxes, composition profiles, and molar concentrations of binary gas systems could be measured with the experimental apparatus.

PROCEDURE

Development of Operating Procedure

Although the apparatus and measurements of this project were not radically new, no prior detailed reports of similar work or equipment existed. Thus some early effort was devoted to developing good operating techniques.

One of the more critical parameters of this experimental work was diffusion cell temperature. The Thermotrol controller used was capable of very precise response and heat input rates. Consequently the cell temperature was determined for various controller settings in the range of temperatures of interest. An iron-constantan thermocouple at the end of a long glass probe was used to obtain temperatures within the cell. With chloroform in the cell well approximately 1 cm deep the temperature control unit was operated at a given setting for several hours continuously. Then the thermocouple bead was placed within the liquid, just above the surface, and then higher up in the cell vapor portion. Potentiometer readings were made to within $\pm$ 0.002 mv and the potentials converted to temperature with National Bureau of Standards tables. By repeating this procedure over a range of controller settings, thermocouple positions, and extended exposure times, it was verified that the cell interior was isothermal to within $\pm$ 0.2^{o}C. Also these data provided a calibration curve from which cell

temperatures could be selected to within $\pm$ 0.4°C.

Another process variable which required selection was the velocity of gas through the cross head unit. Since any reasonable flow rate through the straightening vanes would be laminar, a flow rate which would assure stable end conditions at the Arnold cell top, yet economize gas usage was sought. By observing various diffusing vapor composition profiles at different cross head flow rates it was found that for flows of approximately 1 L/min through the cross head the diffusing vapor mole fraction would become zero just below the cell top.

Optical Subsystem Alignment

After assembling the optical subsystem it was necessary to integrate and precisely align all units of the experimental system. The collimator-lamp units were arranged along the collimator's horizontal optical axis to produce a narrow beam of parallel wave fronts striking mirror M_{10} of the interferometer unit. Then the two interferometer beams, the active and the passive, were aligned to be precisely coincident and create an interference pattern.

Alignment of the interferometer took place in several stages. With the interferometer in place around the diffusion cell the beam from the collimator was directed into prism P_1 (see Figure 6). The active branch was adjusted to traverse the cell horizontally with six

passes through the M_1, M_2, M_3, M_4 mirror array. Further adjustments were made to the active branch components until that beam emerged from prism P_2 and entered the viewing telescope's optical axis.

Following this adjustment of the active branch, the passive branch was brought into alignment. This took place by successive adjustment of the passive branch components until this branch beam entered the viewing scope coincident with the active branch. This procedure then resulted in an interference pattern of sodium D light of circular fringes characteristic of a Michelson interferometer and localized at infinity (Ditchburn, 1963).

Developing Composition Profile Measurements

Several test sequences were performed to perfect the operation of the system in making measurements of composition profiles. A controller setting was selected and the heating unit started to bring the diffusion cell to 55°C. The solvent delivery unit was charged with chloroform and purged of air bubbles in the line, leaving a liquid depth in the cell well of about 0.7 cm. Air was ducted through the cross head at about 1 L/min and several hours allowed to elapse for the system to reach steady state. At this time the composition profile was measured.

Various cell traversing speeds by the interferometer unit

ranging from 0.01 cm/min to 6 cm/min were tried. Both downward and upward progression of the interferometer were tried as well as several modes of reversal and retracing. The ability to accurately view and count fringe shifts for these various procedures was noted and the method with the best accuracy and reproducibility was selected. The method established as standard from this effort was as follows:

1. Start traverse of cell from top, measuring interferometer initial position with a cathetometer.
2. Begin downward traverse by smooth operation of the jack-screw at a traversing rate of about 4 to 5 cm/min.
3. When a fringe miscount or pattern blur was encountered, downward progression was stopped, interferometer position measured, and interferometer unit raised several centimeters before resumption of downward movement.
4. Fringe shifts were counted as plus or minus movement of successive minima past viewing telescope cross hairs.

Diffusing Gas Composition Profile Measurements

Because the composition profiles of the air-chloroform system obtained in the previous development sequence appeared anomolous, several binary gas systems were investigated. A series of runs covering variation of temperatures and binary systems were carried out to evaluate the precision and validity of the experimental system.

For the first experimental run the solvent delivery unit was thoroughly cleaned and purged, then filled with reagent grade benzene. The temperature control unit was started and the Arnold cell brought up to an operating temperature of 65.2°C. Dried compressed air was ducted through the cross head at about 0.7L/min. After an elapsed time at these conditions of 18 hours, the composition profile was measured using the standardized method of operating the interferometer unit. Five hours later another measurement of the composition profile measurement was made, and no changes to the system were made in the intervening time.

At a later date this same general method was followed in obtaining the composition profile for benzene-nitrogen system at 47.5°C. During these benzene system experimental runs and all subsequent runs with other systems, the prevailing barometric pressure was periodically checked in order to obtain a time averaged total pressure in the cell.

In addition to the benzene systems, chloroform-air at room temperature and chloroform-nitrogen at 50.8°C and at 60.5°C were examined. The procedure used to obtain the composition profiles was the same standard one developed earlier. The chloroform charged to the solvent delivery unit for these runs was reagent grade. These chloroform diffusing gas systems were observed in order to gain a comparison of these results to the results of Prabhu (1966) and

thereby thoroughly evaluate the applicability of this experimental approach of obtaining gas phase diffusivity.

At the conclusion of each of these individual system/temperature runs the temperature of the cell solvent liquid was measured with the thermocouple probe. This provided an accurate determination of cell temperature and was compared to the controller calibration curve. From these temperature data and barometric pressure data, the vapor pressure of the solvent was calculated, and by assuming an ideal gas behavior, the gas molar concentration and refractive index could be calculated. That information along with the chart recording of the interferometer fringe shift-position measurements allowed the composition profiles to be calculated by the relationship expressed in equation (11).

Mass Flux Measurements

Because the solvent delivery unit experienced small, but bothersome leakage through the seals and tubing, a special procedure was employed to obtain mass flux data. Using the special insert cup filled with reagent grade solvent a series of evaporation rate measurements were made for benzene-nitrogen and chloroform-nitrogen.

To obtain the data for the chloroform-nitrogen system the insert cup was filled with approximately 11 ml of chloroform at room temperature and the combined weight determined to within $\pm$ 0.01 gram.

Then the insert was lowered into the previously heated cell and suspended by a small diameter wire a distance partway down the cell. The diffusion cell subsystem was then allowed to operate at steady state for about 18 hours at a temperature of 50.8°C, the same conditions as during the earlier composition profile measurements. At the end of this time period the insert was withdrawn and immediately reweighed. This procedure was repeated with the insert suspended in the Arnold cell at several positions and with the weight loss, elapsed time, cell cross sectional area, and molecular weight data a series of mass flux values were computed. These data for the insert at several positions could be extrapolated to the point at which the liquid surface existed during the composition profile measurements. A like procedure was followed with the benzene-nitrogen at 47.5°C.

Mass flux data obtained in this manner could then be used for the same conditions as prevailing during composition profiles to calculate the gas phase diffusivity at any particular composition of the binary gas system. From these composition profiles, combined with the ideal gas law approximation for the molar concentration, the concentration gradients for the diffusing gas could be calculated graphically yielding values for $(d/dz)(y_A C)$. This term along with the values for the other terms in equation (4) (mass flux and mole fraction) were then sufficient to allow a determination of diffusivity to be made.

The results of these calculations were then compared to the results of Prabhu's (1966) experimental work to evaluate the applicability of this experimental method and meet the project objectives.

RESULTS

Composition Profile Measurements

After the experimental data had been processed into the form of composition profiles and mass fluxes, the results appeared to be contrary to expected Arnold cell behavior. Since the experimental measurements which enabled composition profiles to be calculated were reproducible with little variation, the objective of demonstrating such direct measurements was met. Although the measurements of mass flux appeared to be experimentally consistent, some question as to their validity exists. For this reason, the gas phase diffusivity which depends upon a correct value of mass flux in its computation might be questionable.

For ease of comparison, the composition profiles were reduced to a dimensionless form of $y(z)/y_{eq}$ versus z/L. The results in this form for the several binary gas systems studied are shown in Figures 8, 9, and 10. For some of these systems the number of data points associated with a particular composition profile exceeds 150. It would be impossible to include all such data points in these figures, so for clarity only intermittent points are shown. However, all the composition data points are included in Figure 8 for the methanol-nitrogen system. The procedure used to calculate these profiles from the actual recorded experimental data is shown in Appendix B,

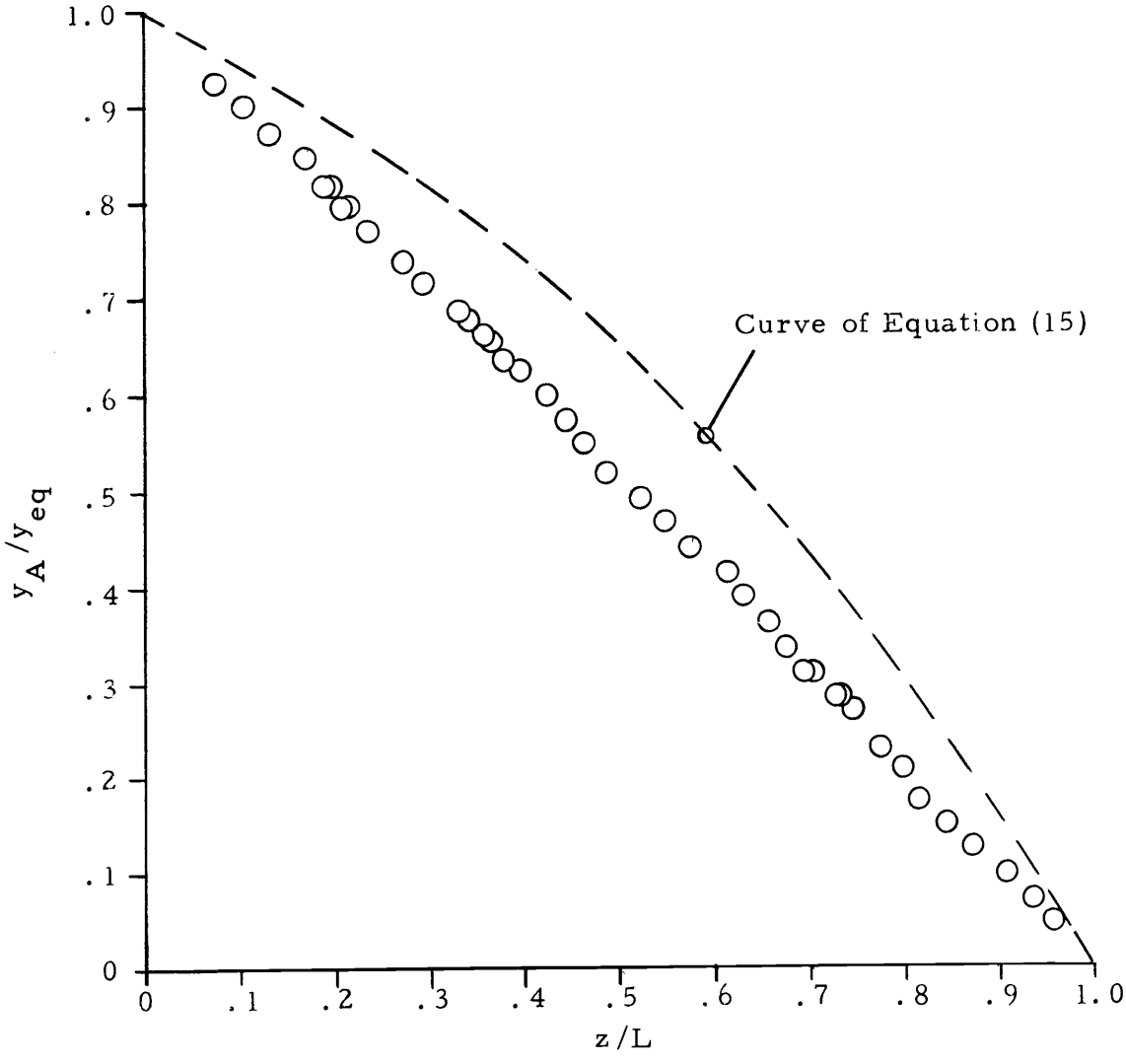

Figure 8. Composition profile for methanol-nitrogen system at 55°C, 1 atm (all data points shown).

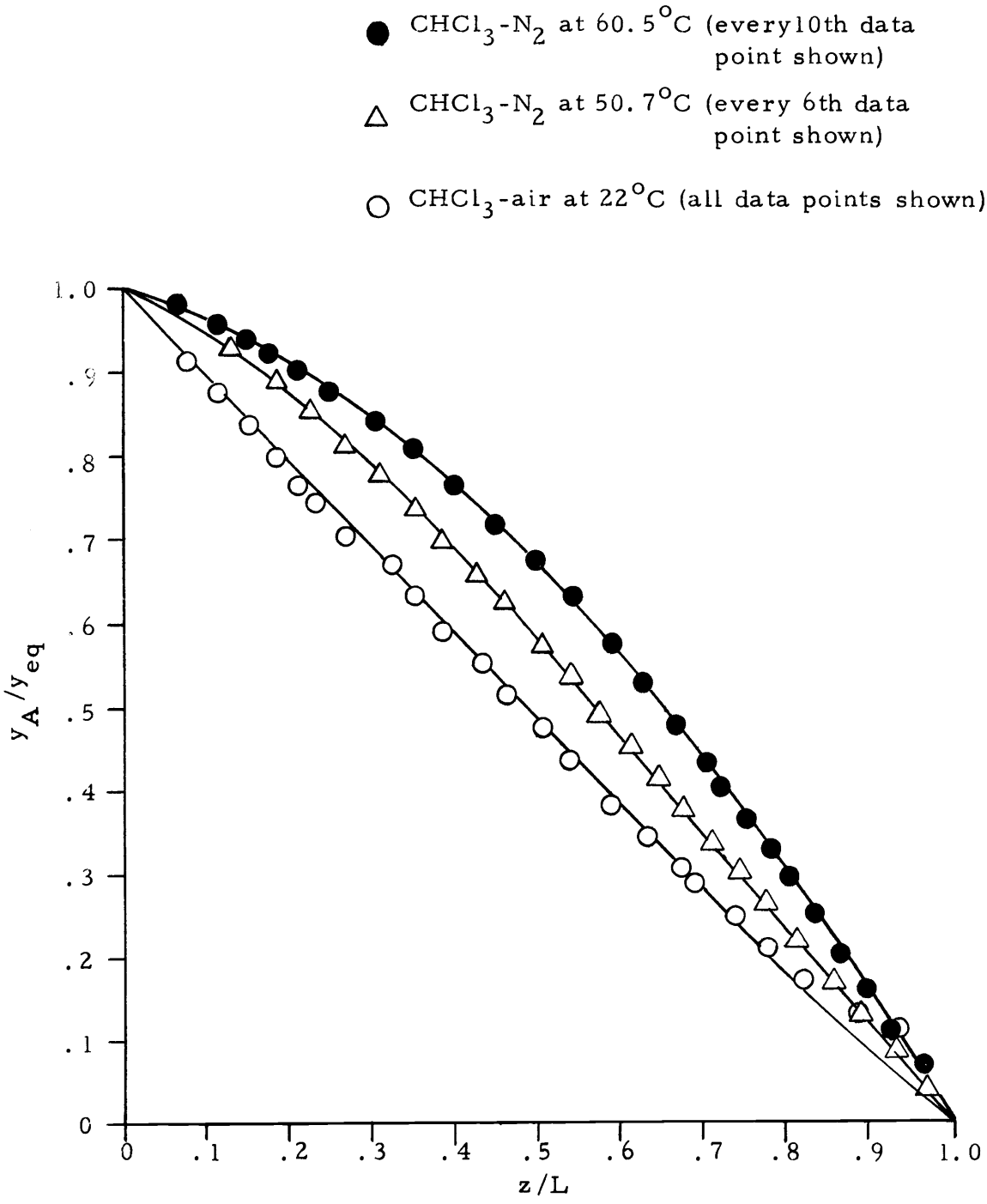

Figure 9. Composition profiles of chloroform-air and chloroform-nitrogen systems.

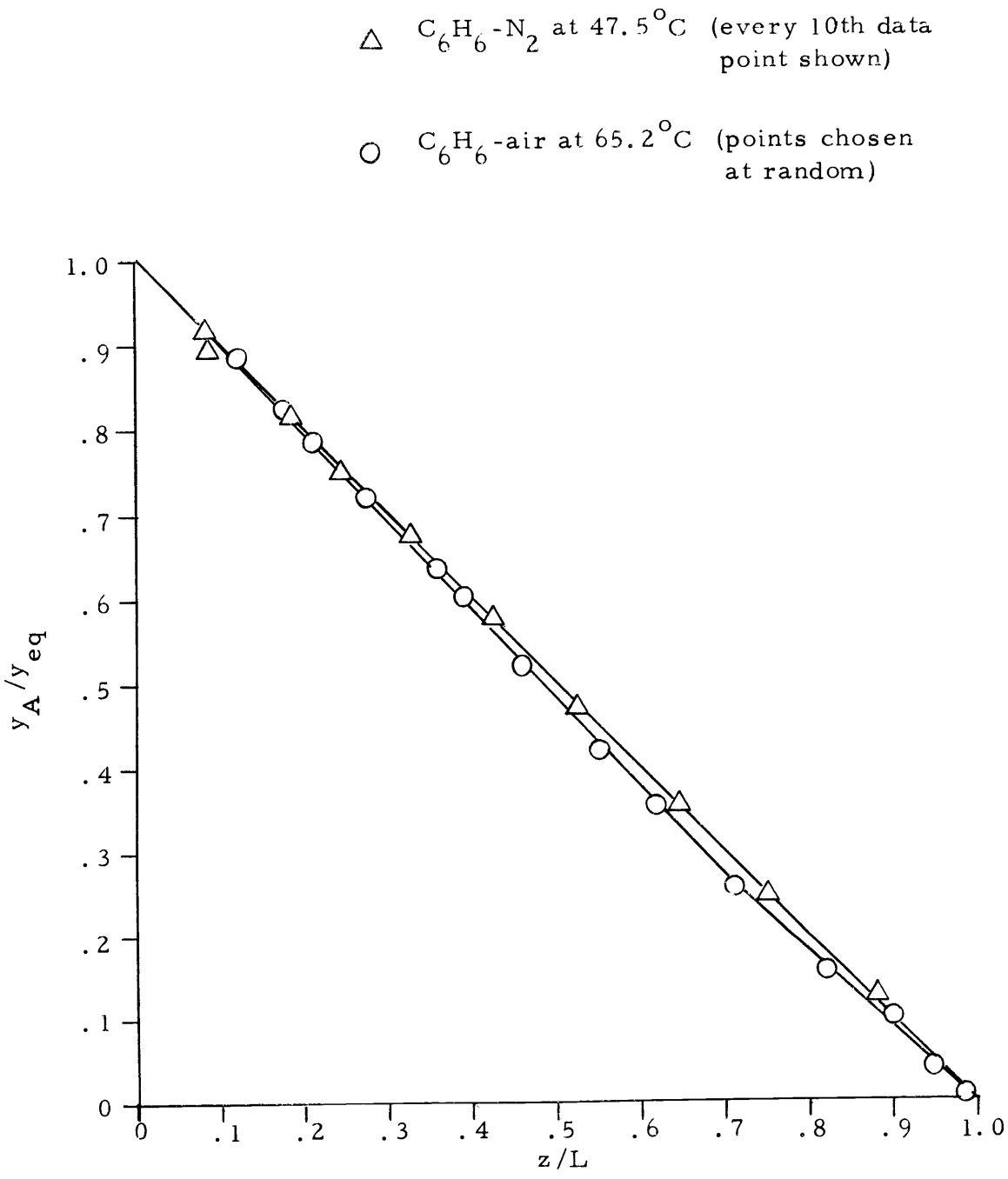

Figure 10. Composition profiles of benzene-air and benzene-nitrogen systems.

Processing Composition Profile Data. An indication of the data scatter can be seen in Figure 8 and in Figure 15 which shows a portion of the chloroform-nitrogen system at 50.7°C.

It can be clearly seen from Figure 10 that the composition profiles for the benzene-nitrogen systems are very close to straight lines. If it can be assumed that the actual composition profile existing within the cell was indeed precisely linear, then the experimental accuracy in measuring that profile can be determined. Unfortunately, common gas sampling and analyzing methods such as chromatography or thermal conductivity are not sufficient to detect gas composition at a specific point within the cell with the precision required to independently check the optical subsystem's operation. Thus it can only be assumed that the optical subsystem measured composition profiles within the design tolerance and that the deviation and variation about a perfectly linear profile represent an experimental error. The results of such an analysis are shown in Table 2.

When the diffusivity of a binary gas system is considered a constant, it has been shown (Bird et al., 1960) that equation (1) applied to an Arnold cell can be solved to give the composition profile as equation (15).

$$\left(\frac{1-y_A}{1-y_{eq}}\right) = \left(\frac{1}{1-y_{eq}}\right)^{z/L} \qquad (15)$$

This is the composition profile resulting from integration of Fick's

Table 2. Precision of concentration profile measurements.

	Chloroform-nitrogen 50.8°C (mole fraction)	Benzene-air 65.2°C (mole fraction)
Maximum scatter of observed y_A from smoothed data	±.005	±.007
Nominal scatter of observed y_A from smoothed data	±.003	±.002
Maximum variation between $y_A(z)$ for repeated runs	±.014	±.008
Nominal variation between $y_A(z)$ for repeated runs	±.009	±.004

law in the form of equation (1) and does not involve the diffusivity, so long as it is a constant. Prabhu (1966) determined that $\mathcal{D}_{AB}$ for the methanol-air system at 55°C was very closely approximated as a constant 0.162 cm^2/sec. Therefore the composition profile predicted by equation (15) for the methanol-nitrogen system with a constant diffusivity is shown as a dotted line on Figure 8, and it differs markedly from the profile which was observed in this project. A similar profile predicted by equation (15) for a constant diffusivity case could be plotted for the benzene-nitrogen systems which again would differ markedly from the observed linear profiles.

Both the theoretical design basis and the operation of the optical subsystem were examined to assure that the treatment of the experimental data was proper. This examination proved that the optical subsystem was indeed measuring the composition profile existing within the diffusion cell. However, implicit in the development of equation (4) and interpretation of the experimental results is the assumption that the mass flux of component A, the diffusing one, is constant throughout the length of the cell. If there was a leakage of vapor through the glass to metal seals along portions of the cell length, then a perturbed composition profile would exist. The optical subsystem would accurately measure this profile, but it would not be the profile of an Arnold cell with constant mass flux. Results of the mass flux measurements required to calculate diffusivities indicate

that the assumption of a constant mass flux is questionable.

Mass Flux Measurements

There are several ways of analyzing the mass flux data listed in Appendix D. A method described previously consists of plotting the data graphically in order to eliminate the upper end turbulence and the liquid meniscus shortening of the apparent diffusion path length (Lee and Wilke, 1954). In analyzing the data in this manner the reciprocal of mass flux, $1/N_A$, is plotted against the actual distance from liquid meniscus bottom to the cell top. With the data for mass flux obtained for various distances from liquid to cell top, all for the same conditions of temperature, pressure, and cross head flow rates, an intercept of $1/N_A = 0.$ is found. The interpretation of this distance is the end effects correction, and the remaining distance from this intercept point to the actual liquid level is the pure diffusion path length.

Another approach to analyzing the mass flux data was used in this project. With the mass flux data obtained from the weight change and elapsed time for the insert cup at various distances below the cell top, an extrapolation of the computed mass fluxes was made to the point at which the liquid level existed during the composition profile measurements. This method of analysis provided a value of mass flux, N_A, which was then used with the composition profile data in

equation (4) to calculate diffusivity at various point values of composition. The mass fluxes for the two binary gas systems for which these measurements were made are listed in Table 3, and the values correspond to the liquid at the position during the profile measurements.

Table 3. Estimated mass fluxes during composition profile measurements.

System	Temperature (^{o}C)	Pressure (atm)	Mass flux (moles /cm^{2} hr)
Benzene-nitrogen	47.5	1.0	.00030
Chloroform-nitrogen	50.7	1.0	.00073

The results of plotting $1/N_A$ versus distance from top to liquid surface yielded an end effects correction value of about 9 cm; in other words, a computed diffusion path, L, of about 22 cm. However, it was experimentally observed that the composition profile was considerably longer than this with the point of zero mole fraction of component A near and slightly below the cell top, not some 9 cm below. For this reason it was concluded that this treatment of the mass flux data from this project to establish an end effects correction was invalid, implying that the assumptions made in doing so were not valid in this case.

Calculation of Diffusivity

When all data points for the chloroform-nitrogen system at 50.7°C were plotted graphically the slopes of the curve, dy/dz, at various y_A values were determined. Using these data in conjunction with the mass flux value as listed in Table 3, the gas pair diffusivity[5], $\mathcal{D}_{AB}$, was computed from equation (4). The variation of diffusivity with composition for the chloroform-nitrogen system computed in this manner is shown in Figure 11.

A similar procedure was followed in determining the diffusivity of the benzene-nitrogen system at 47.5°C. In the case of this system, the composition profile very closely approximated a straight line yielding a composition gradient of:

$$\frac{dy}{dz} = 0.0127 \ \frac{\text{mole fraction}}{\text{cm}}$$

With this constant value for dy/dz in equation (4), and with all other parameters constant, diffusivity varies directly with the term $(1-y_A)$. This variation with composition is shown in Figure 12.

In order to obtain a further evaluation of the results of this experimental work, a comparison of the chloroform-nitrogen system at 50.7°C to Prabhu's (1966) results was made. From the diffusivity as a function of chloroform mole fraction, determined empirically

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[5] This value of $\mathcal{D}_{AB}$ corresponds to the expression $F(X_A)$ as defined and used by Prabhu (1966).

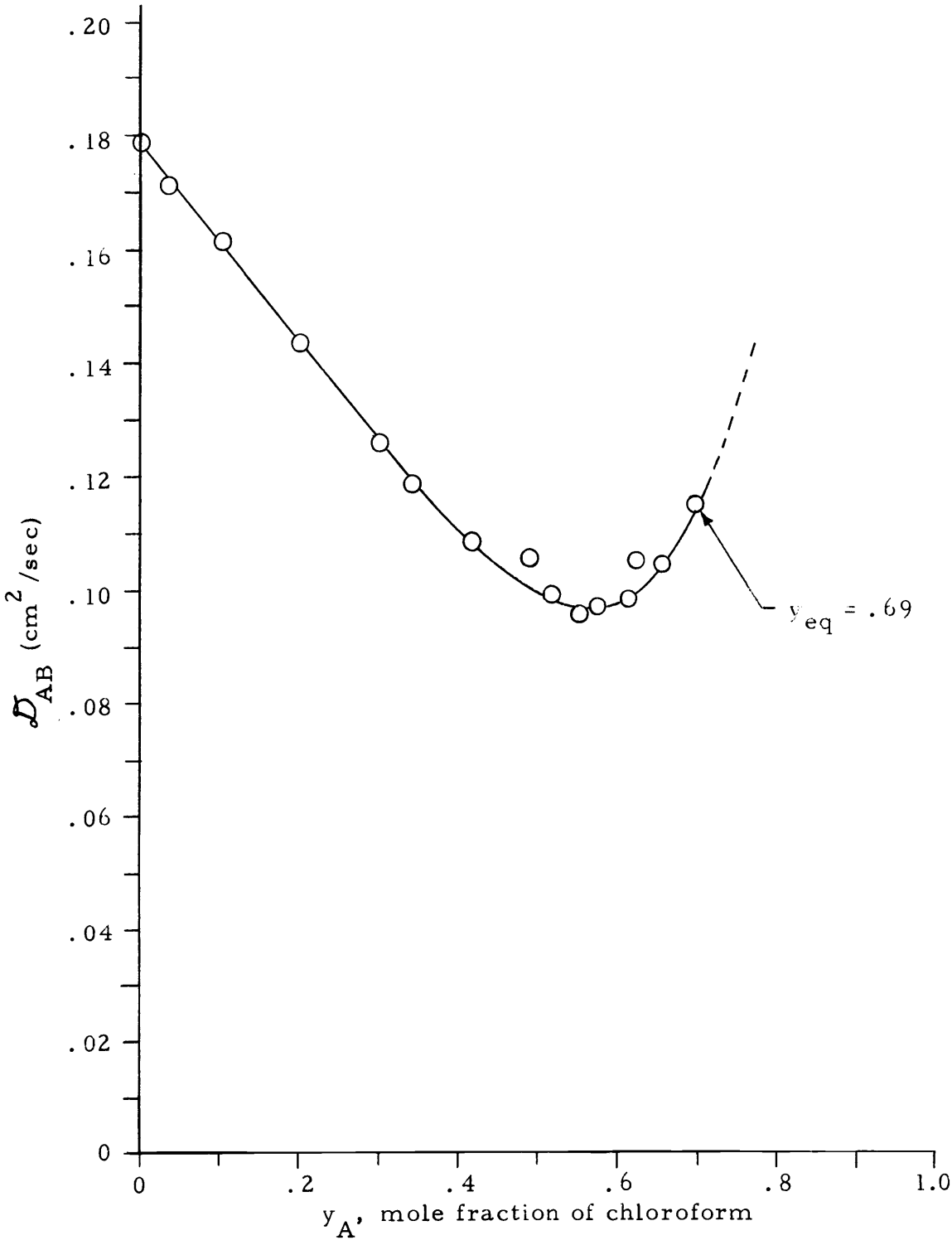

Figure 11. Calculated diffusivity of chloroform-nitrogen at 50.7°C, 1 atm.

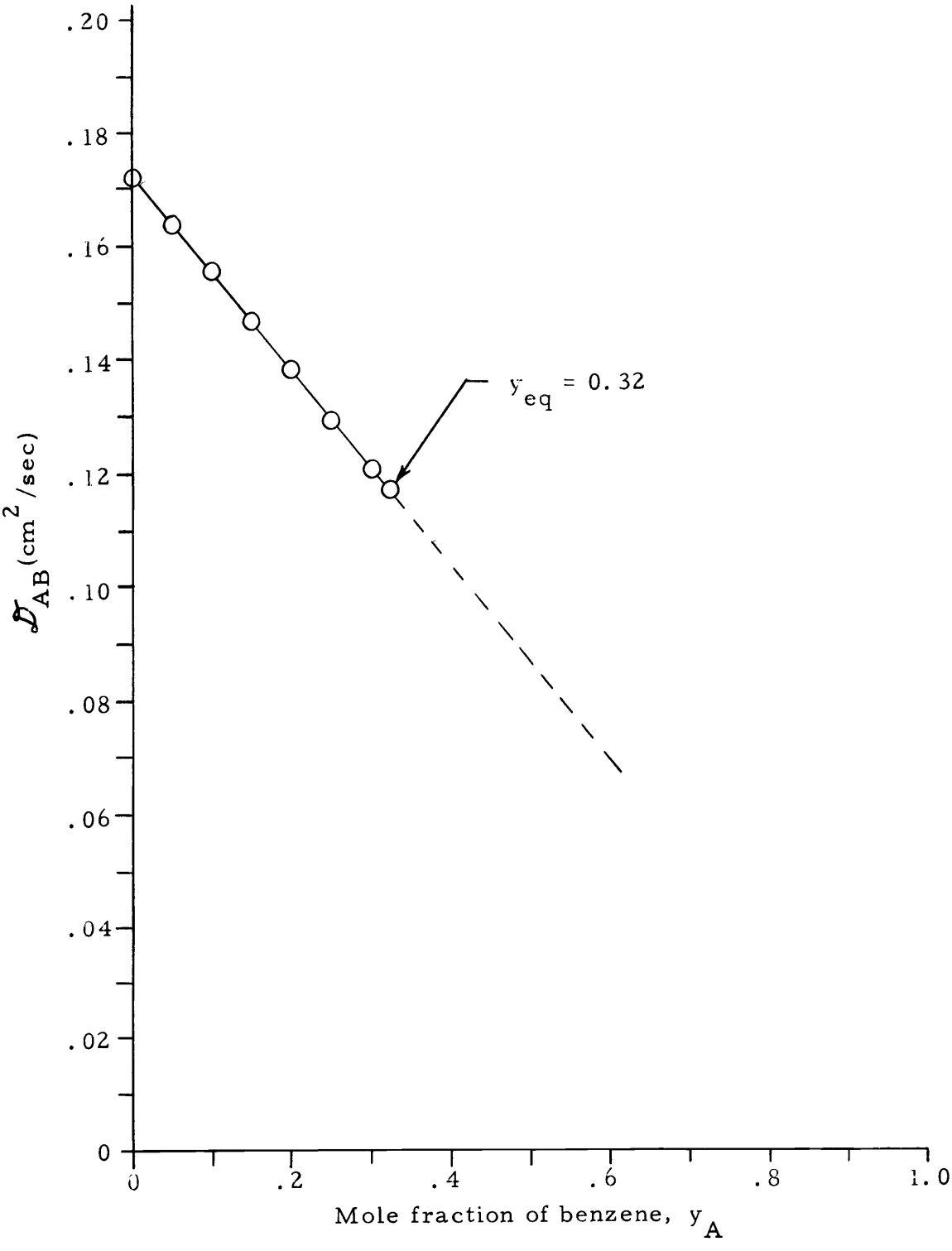

Figure 12. Calculated diffusivity of benzene-nitrogen at 47.5°C, 1 atm.

from Figure 11, a numerical integration of Prabhu's defining equation for average diffusivity (equation (16)) was made.

$$\overline{\mathcal{D}}_{AB} = \frac{\int_{y_{A1}}^{y_{A2}} \frac{\mathcal{D}(y_A)}{1-y_A}\, dy_A}{\ln\left(\frac{1-y_{A2}}{1-y_{A1}}\right)} \qquad (16)$$

The results of this integration for the experimental diffusivities from this project and a comparison to Prabhu's (1966) results are shown in Table 4. In this case y_{A1} is y_{eq}.

Table 4. Concentration average diffusivity for chloroform at 50°C and 1.0 atm.

y_{A2}	$\overline{\mathcal{D}}_{AB}$	
	(this work)	(Prabhu)
.566	.111 cm^2/sec	.115 cm^2/sec
.435	.111	.111
.364	.112	.110
.257	.115	.108
.174	.119	.107
0	.128	.106

Although the results in both cases indicate a variation of diffusivity with composition of the order of ten percent, Prabhu found the diffusivity to increase with increasing concentration of the heavier component, chloroform. The results of this project indicate the opposite trend.

Evaluation of Results

The gas phase diffusivities calculated from the experimental data of this project are of questionable accuracy. Unfortunately, the source of the error could not be definitely established. The operation of the optical subsystem to detect composition changes was proven by observing the fringe shifts caused by a change of known composition. This was done by raising the temperature without the cell in a stepwise manner, thus causing a known increase in solvent vapor y_A throughout the stoppered cell. In addition, the physical optics fundamentals upon which the design is based are sound and very well established. For that reason it was concluded that the optical subsystem was measuring an actual, but possibly perturbed composition profile.

Because of the difficulty experienced with leakage of the solvent delivery unit and the unexpectedly high mass fluxes measured with the insert cup, the assumption that all solvent evaporating was removed from the cell solely by diffusion is questionable. The polymeric material which sealed the cell at the corners and along the length of the glass sides' edges was resistant to disintegration in the solvents used, but cannot be considered impermeable. However, no data on the permeability of the solvent molecules through these materials existed and equipment was not available to detect and measure the size

of any leaks through the glass-metal seals in the region where vapors were diffusing upward, and possibly outward.

Other possible explanations for the anomolous composition profiles may be the existence of very weak turbulence in the upper portion of the cell or a non-uniform upward flow of diffusing vapor. If the cell which had a cross sectional area of 4.92 cm^2 exceeded some critical configuration, then the flow of vapors may not have been uniformly distributed across the cell. Turbulence induced by flowing gas across the cell top is assumed to have only a minimal effect adjacent to the cell top, as discussed by Lee and Wilke (1954), but would perturb the profile considerably if the effects extended deeply into the cell. The steadiness of the interference pattern at all positions, even near the top, and the uniformity of the observed profiles tend to negate that possibility.

Of course, it should not be deemed impossible that the observed composition profiles which appear anomolous are very nearly the correct ones for an Arnold cell. The composition profiles in a normally operating Arnold cell have not been verified experimentally to any degree of precision prior to this project. The usual treatment of experimental results of Arnold cell work is based upon the assumptions that the diffusivity at the prevailing conditions is a constant and that equation (2) truly represents the mass transport taking place due to pure diffusion. The abnormally high mass fluxes measured in this

project would indicate that the cell used was not a true Arnold cell, but the inability to pinpoint a cause for the higher fluxes and almost precisely linear composition profiles leaves the situation in doubt. For these reasons and because the results of Prabhu (1966) showed that for mild conditions of temperature and pressure diffusivity can be a significant function of gas system composition, a much further study of Arnold cell behavior and data interpretation is warranted.

Nevertheless, one objective of this project in demonstrating that a movable optical interferometer can be readily combined with an Arnold diffusion cell was met. Composition gradients established at steady state conditions were accurately measured by means of an unsophisticated Mach-Zender interferometer detecting changes in refractive index. Such composition profiles were measured with sufficient accuracy to graphically obtain values for the gradient dy/dz. If the mass flux associated with those point values of composition and concentration gradient could be reliably known with equal accuracy, then values of gas phase diffusivity at any particular point value of composition could be computed.

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APPENDICES

APPENDIX A

LIST OF SYMBOLS

Axx	Cross sectional area	cm^2
C	Gas molar concentration	moles $/cm^3$
E	Electric field vector of light	nt. /coul
I_{fringe}	Pulse from counter circuit	(dimensionless)
I_z	Pulse from shaft encoder circuit	(dimensionless)
L	Diffusion path length	cm
M	Molecular weight	g/mole
N	Molar mass flux	moles $/cm^2$ sec
P	Pressure	atm
Q	Number of wavelengths	(dimensionless)
R	Gas constant	$\frac{cm^3\ atm}{mole\ ^oK}$
T	Temperature	^oK
W	Weight of evaporated solvent	g
X	an arbitrary length	cm
c	Velocity of light in vacuum	cm/sec
k	Dielectric constant	(dimensionless)
n	Refractive index	(dimensionless)
s	Optical path through cell	cm
t	Time	sec

v	Velocity of light in a medium	cm/sec
y	Mole fraction in gas phase	(dimensionless)
z	Distance in diffusion direction	cm
$\mathcal{D}_{AB}$	Binary molecular diffusivity	cm^2/sec
Δ	Change in a quantity	(dimensionless)
ϵ_0	Electrical permittivity of vacuum	$coul^2/nt.\ m^2$
μ_0	Magnetic permeability of vacuum	weber sec/coul m
ν	Frequency of monochromatic light	cycles/sec

Subscripts

A	Component A of binary gas mixture
B	Component B of binary gas mixture
eq	Value at equilibrium conditions
0	Reference point value

APPENDIX B

PROCESSING CONCENTRATION PROFILE DATA

Source of Data

System parameters of temperature, pressure, elapsed time, weights, and cross head flow rate noted from appropriate instruments and hand recorded on data sheets. Interferometer output data obtained from instrumentation subsystem chart recorder.

Interpretation of Chart Recording

From the chart recordings which appeared as shown in Figure 14, interferometer and accompanying fringe shifts were determined as:

$$Z = Z_0 + (0.03175 \frac{cm}{pulse}) \left(\sum_{Z=Z_0}^{Z} I_z \text{ pulses} \right),$$

and

$$y = y_0 + \left(\frac{4.195 \times 10^{-6}}{n_A - n_B} \quad \frac{\text{mole frac}}{pulse}\right) \left(\sum_{Z=Z_0}^{Z} I_{fringe} \text{ pulses} \right)$$

Position Z_0 is determined by using a cathetometer and y_0 is determined by extending the curvature of the measured profile to the liquid surface, at which $y = y_{eq}$ as determined from vapor pressure data and barometric pressure. The pulses, I_z and I_{fringe}, are generated by the electronic circuit shown in Figure 13.

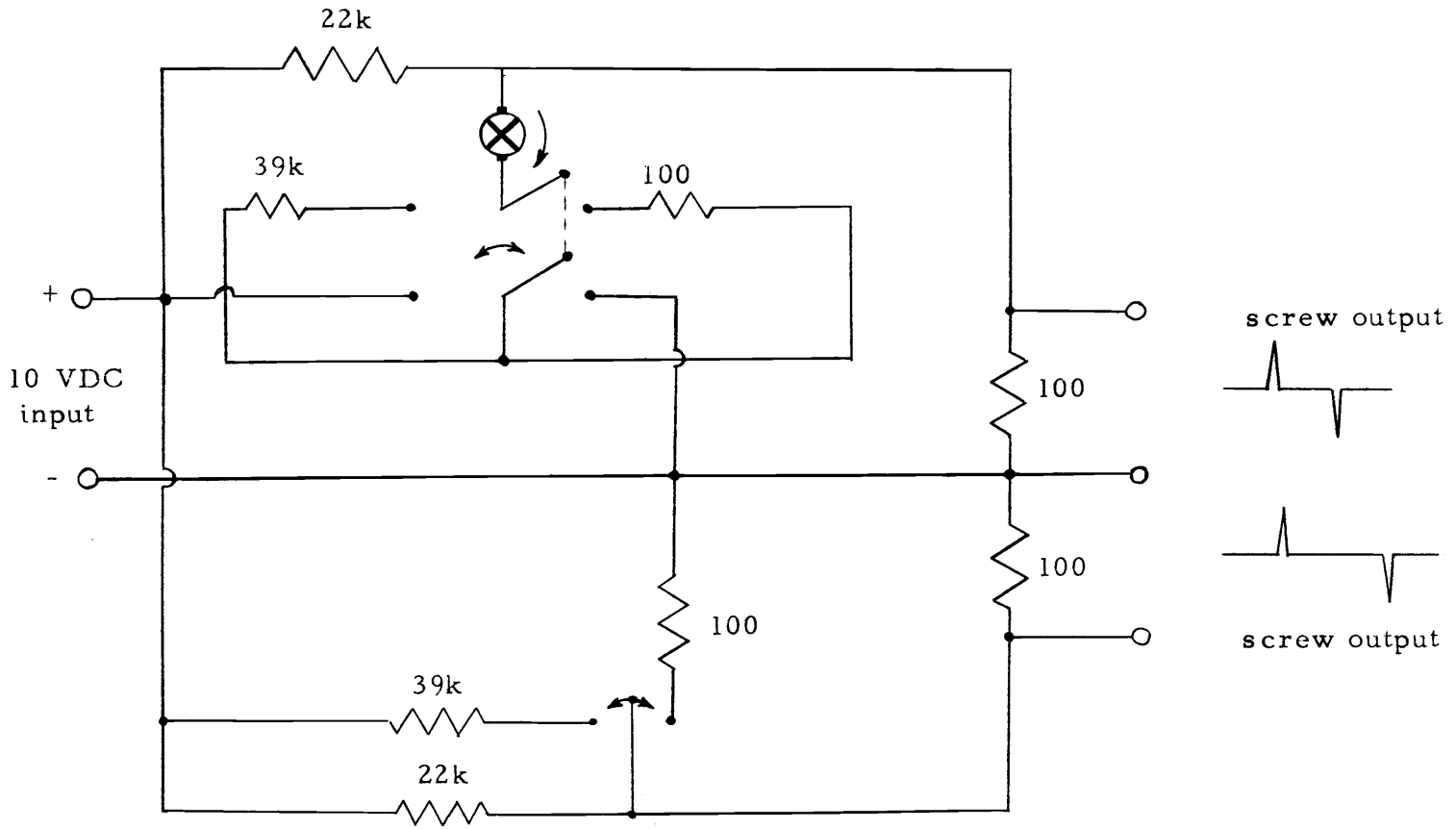

Figure 13. Counting pulse generating circuit.

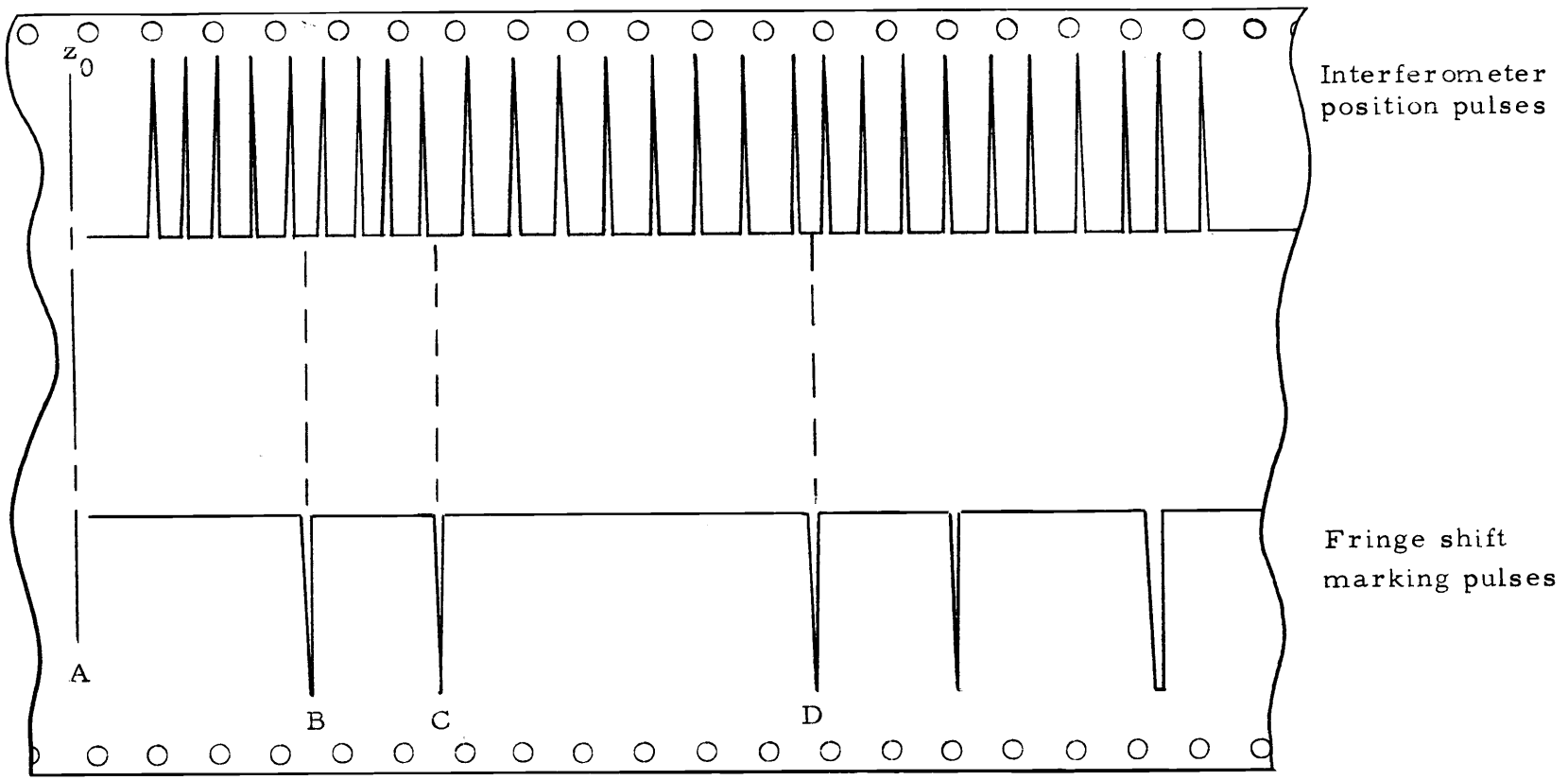

Figure 14. Segment of pulse recording chart for chloroform-nitrogen system at 50.7°C.

Sample Calculation

From Figure 14, point z_0 is 10.15 cm (point A). The second fringe shift minima crosses the viewing telescope vertical cross hair at point C where z is:

$$z = 10.15 \text{ cm} + 0.03175 \times 9 \text{ pulses} = 10.44 \text{ cm}$$

and a mole fraction change at these conditions is:

$$\Delta y = \frac{4.195 \times 10^{-6}}{1.00123 - 1.00025} = .00435 \ \frac{\text{mole frac}}{\text{fringe shift}}$$

Scatter of Data

When the calculations are extended to all the interferometer data of the complete cell traverse, the data scatter would appear as in Figure 8 for the methanol-nitrogen system and Figure 15 for the chloroform-nitrogen system.

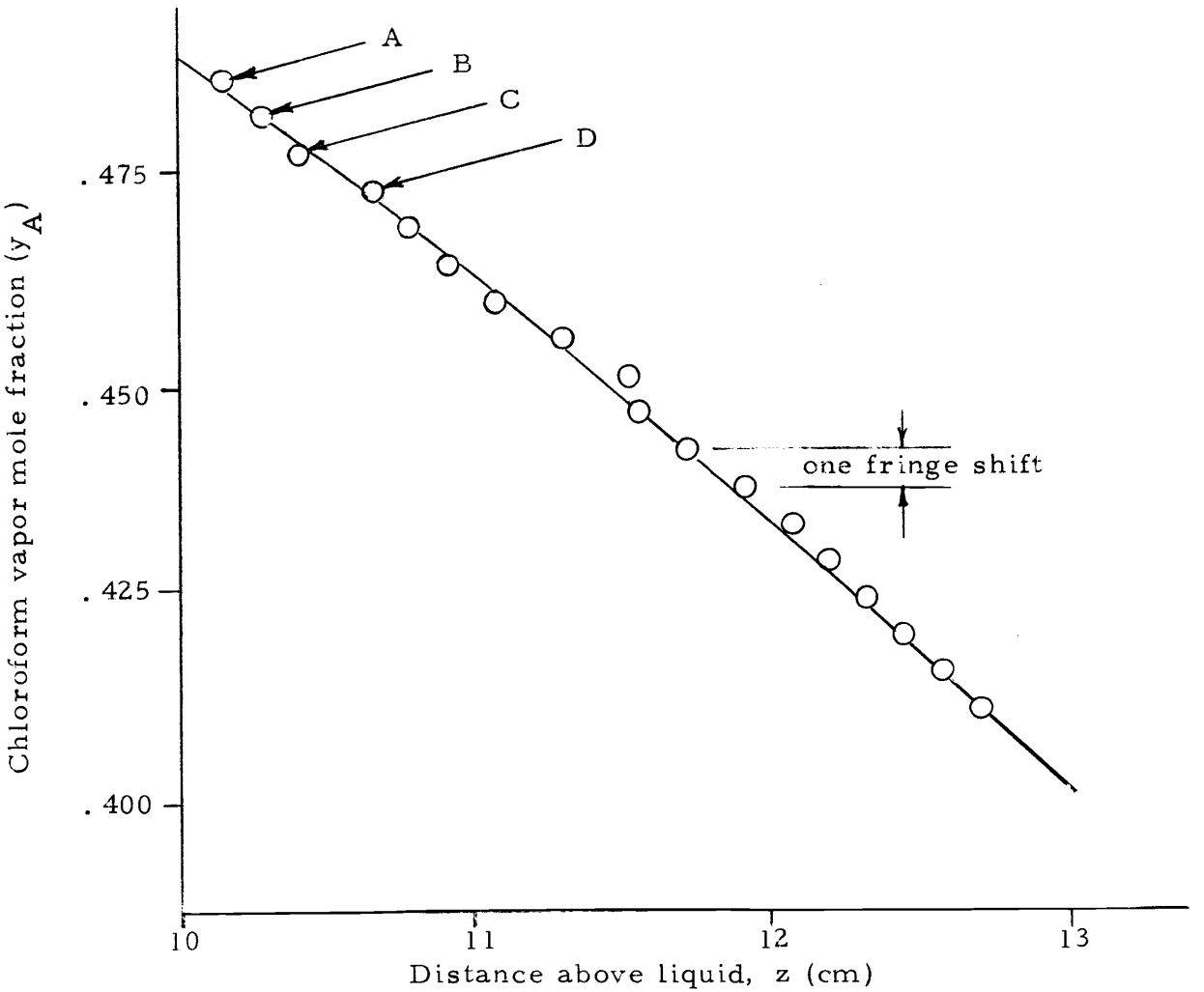

Figure 15. Segment of $CHCl_3$-N_2 composition profile at 50.7°C.

APPENDIX C

PHYSICAL PROPERTY DATA

Table 5. Physical properties of diffusing components.

Property	Air	N_2	C_6H_6	CH_3OH	$CHCl_3$
Molecular weight	29	28	78.11	32.04	119.39
Liquid density[1], g/ml	-	-	0.879	0.792	1.495
Refractive index[1] (gas at 0°C, 1 atm)	1.0002926	1.000296	1.00176	1.00058	1.00145
Vapor pressure (published values[2])					
100 mm Hg	-	-	299.3°K	294.4°K	283.6°K
200	-	-	315.4	308.0	299.1
400	-	-	338.8	323.1	315.9
760	-	-	353.3	337.9	334.5
(estimated vapor pressures[3])					
165	-	-	-	-	295
246	-	-	320.7	-	-
462	-	-	338.4	-	-
512	-	-	-	328.1	-
525	-	-	-	-	324.0
745	-	-	-	-	333.7

[1] Data from Hodgman (1961).

[2] Data from Perry (1963).

[3] Values estimated from a linear plot of ln P^o versus 1/T using data from Perry (1963).

APPENDIX D

Table 6. Experimental data.

Experimental run	1	2	3	4	5	6
Binary gas system	methanol/ nitrogen	benzene/ air	benzene/ nitrogen	chloroform/ nitrogen	chloroform/ air	chloroform/ nitrogen
Cell temperature (^{o}C)	54.9	65.2	47.5	50.8	22.	60.5
Cell pressure (mm)	757	756	758	760	759	759
Solvent vapor equilibrium mole fraction (y_{eq})	.68	.608	.322	.690	.217	.98
Apparent diffusion path, L (cm)	27.69	27.81	25.27	26.42	27.56	31.8
Time before profile measurement start (hr)	24	18.3	6.5	3.	45.	4.
Duration of measurement (hr)	1.5	.6	.7	.5	.4	1.2
Refractive index difference	0.000236	.00120	.00125	.00098	.00107	.00095
Number of fringe shifts observed	36	157	74	138	42	198
$\frac{1}{\Delta Q}$ ($\frac{\text{mole fraction}}{\text{fringe shift}}$)	0.0178	0.00366	.00353	.00435	.00411	.00442

(Continued on next page)

Table 6. (Continued)

Binary gas system	chloroform/ nitrogen	chloroform/ nitrogen	chloroform/ nitrogen	benzene/ nitrogen	benzene/ nitrogen	benzene/ nitrogen	benzene/ nitrogen
Cell temp. (^{o}C)	50.7	50.8	50.8	47.5	47.5	47.5	47.5
Cell pressure (mm)	760	760	760	758	758	756	759
Weight change of solvent cup (grams)	9.68	15.2	9.82	2.43	1.93	5.27	3.13
Position of insert cup from cell top (cm)	28.0	20.5	25.5	28.0	15.0	18.5	25.0
Duration of mass flux measurement (hr)	18.62	16.25	18.33	18.78	6.58	18.67	20.42

APPENDIX E

MISCELLANEOUS SYSTEM SPECIFICATIONS

Table 7. Miscellaneous experimental data.

Barometric pressure average fluctuations (mm Hg)	± 3
Compressibility factors of solvent vapors	1.0 + .00 - .017
Cross head vane section open area (cm^2)	1.94
Cross head vane wetted perimeter (cm)	57.
Heating fluid flow rate (L/min)	5.32
Mass flux cup dimensions (cm)	2.1 x 2.3 x 3.2 deep
Optical path length (total) through cell, s (cm)	14.05
Split light beams length (cm)	50.2
Telescope magnifying power	20X
Width of cell covered by active branch passes (cm)	1.8