

## Subscripts

*h* refers to less volatile component  
*l* refers to liquid phase  
*v* refers to vapor phase  
*c* refers to critical conditions of more volatile component  
*ch* refers to critical conditions of less volatile component  
*r* refers to reduced conditions relative to the critical point of more volatile component

## Superscripts

<sup>o</sup> refers to saturation conditions of pure, more volatile component  
 — refers to average value of quantity below bar

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RECEIVED for review November 27, 1953.

ACCEPTED May 5, 1954.

# Measurements of Vapor Diffusion Coefficient

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THE method used in this study was originated by Stefan (17, 18) and used extensively by other investigators (7, 12, 21, 22, 24, 25). One of the components, in the liquid state, is placed in the bottom of a vertical tube. With the tube and liquid maintained at constant temperature, the second component, a gas, is passed over the top of the tube at a rate sufficient to keep the partial pressure of the vapor there at a value essentially corresponding to the initial composition of the gas—i.e., zero in the case of vapor-free gas. The gas rate must be low enough to prevent turbulence at the mouth of the tube.

The general theory of the method may be presented by considering a tube to be filled with liquid (designated as component A), so that the gas-liquid interface is located at a distance  $x$  from the top of the tube, as shown in Figure 1, *a*. In the steady state the rate of vaporization is given by the well-known equation

$$N_A = \frac{DP\Delta p}{RTp_r x} \quad (1)$$

where

$$p_r = \frac{(P - p_s) - (P - p_0)}{\ln \frac{(P - p_s)}{(P - p_0)}}$$

Background and general limitations of Equation 1 have been reviewed by Wilke (26). The equation is specifically applicable only to the diffusion of one gas through a second stagnant gas. In this case there is a finite hydrodynamic velocity in the tube corresponding to the rate of diffusion of component A. In the derivation of Equation 1 an average uniform hydrodynamic velocity over the tube cross section is assumed, whereas in viscous flow the velocity distribution should be parabolic. Possible error due to this assumption may warrant special study (15).

During diffusion the liquid level falls as vaporization proceeds and  $x$  is not constant. Assuming quasi-steady-state conditions, it can be shown that  $x$  may be taken as the arithmetic average of

values at the beginning and end of the diffusion period and used in conjunction with the over-all average rate of diffusion to give correct values of  $D$  by solution of Equation 1. Thus:

$$N_A = \frac{W_A}{M_A \theta S} \quad (2)$$

$$x = \frac{x_0 + x_\theta}{2} \quad (3)$$

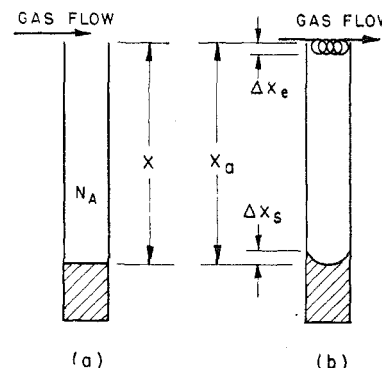


Figure 1. Models for Application of Theory

The assumption of quasi-steady-state conditions usually involves negligible error for measurements at atmospheric pressure—i.e., when the relative change in  $x$  with time is very small.

## APPARATUS AND MATERIALS

The apparatus was constructed somewhat along lines employed by McMurtrie and Keyes (14), utilizing diffusion tubes of larger

diameter than those of most previous studies. Figures 2 and 3 illustrate the diffusion tube and holder and Figure 4 is a flow diagram of the entire apparatus.

The diffusion unit (Figure 2) was made of brass to obtain satisfactory heat conduction into the system from the surrounding constant temperature bath. The upper gas chamber, 8.5 cm. in diameter, was connected to gas inlet and outlet tubes 1.8 cm. in diameter by means of union joints, so that the diffusion tube could be inverted for downward diffusion. Straightening vanes consisting of thin copper plates 2 mm. apart extended from the end of the gas inlet tube to the edge of the diffusion tube to reduce gas disturbance associated with the sudden enlargement of the flow path. The diffusion tube was fitted tightly into a holder which screwed into the bottom of the gas chamber. Two holders were employed for diffusion tubes 1.75 and 0.94 cm. in diameter (Figure 3).

Tube diameters were arbitrarily selected, and other sizes might have been satisfactory. In general, it is necessary to have a large enough diameter to obtain a conveniently weighable evaporation loss in a reasonable time without excessive disturbance inside the tube due to gas flow.

The diffusion unit was connected into the apparatus as indicated in Figure 4.

Gas from a cylinder connected to the surge tank was supplied to the system as required to maintain the total pressure at the diffusion tube constant and slightly above the prevailing atmospheric level. A blower provided continuous recirculation of gas in the system. The diffusion unit was immersed in an oil bath maintained at  $25^{\circ} \pm 0.02^{\circ} \text{C}$ . An electric heater placed in the line leading to the unit brought the gas to within  $1^{\circ} \text{C}$ . of the bath temperature. The gas then passed through a 40-foot coil of  $1/8$ -inch copper tubing immersed in the oil bath which brought the gas entering the diffusion unit to the bath temperature. Rate of gas flow was measured with an orifice meter and controlled manually with a bypass valve at the blower. To prevent saturation with vapor, the gas leaving the diffusion tube was passed through a condensing coil immersed in a large Dewar flask containing a suitable refrigerant.

In experiments with air, gas recirculation and condensation of vapor were not employed; air entering the system was dried in a calcium chloride tower and discharged to the room after leaving the diffusion unit. To eliminate vibration, the blower and stirring motor for the oil bath were mounted independently on the concrete floor of the laboratory. A vacuum pump was employed to evacuate the entire apparatus prior to charging the system with gas.

Liquids used included water, benzene, nitrobenzene, ether, and absolute alcohol. Benzene and nitrobenzene were redistilled. Boiling points, and in some cases freezing points, were measured for all materials and found to agree well with accepted values in the literature.

High purity Freon 12 and helium were used as received from

E. I. du Pont de Nemours & Co. and U. S. Bureau of Mines, respectively. Specified purity was 99.96% or better for both gases.

#### EXPERIMENTAL PROCEDURE

With valves  $V_2$ ,  $V_3$ ,  $V_5$ ,  $V_6$ , and  $V_{10}$  closed (see Figure 4) the whole system was evacuated with the vacuum pump until 29.5-inch vacuum (highest obtainable with this pump) was indicated by the mercury manometer,  $C_1$ . Valve  $V_3$  was opened and the system was filled with the gas used from the gas cylinder to atmospheric pressure. With valve  $V_2$  closed, the system was evacuated once more. The system then was filled again to about 4 inches of mercury positive pressure and the gas in the system analyzed for oxygen. The procedure of evacuation and filling was repeated until the air content of the system was reduced to 0.1% or less. The condensing units were filled with the proper refrigerant (dry ice and acetone when helium was used; dry ice and carbon tetrachloride when Freon was used; and liquid nitrogen for some runs with air). The diffusion tube was filled to a desired level with liquid, stoppered, and weighed. With valves  $V_4$  and  $V_9$  closed, the cover of the diffusion unit was opened, the diffusion tube was quickly inserted into the holder, and the stopper was removed. With the cover replaced, the diffusion unit was immersed in the bath. The electric heater,  $D$ , was turned on. With valves  $V_2$ ,  $V_{10}$ , and  $V_8$  opened the system was flushed with the gas for 10 minutes at the desired flow rate. Valves  $V_2$  and  $V_8$  were then closed. Valves  $V_9$ ,  $V_5$ , and  $V_6$  were opened while the blower was turned on.  $V_4$  was adjusted to obtain the desired flow rate. The time, flow rate, temperature of the bath, atmospheric pressure, manometer  $C_2$  reading (about 3 inches of mercury positive pressure was maintained to prevent leakage into the system), diffusion length, and initial weight of the tube were recorded. The temperature of the gas passing through the condensing unit,  $N$ , was recorded every 2 hours.

At the end of a run, the blower was turned off, valves  $V_4$ ,  $V_5$ ,  $V_6$ , and  $V_9$  were closed, and the diffusion tube was taken out, stoppered, and weighed. The tube was always filled with the same gas when weighed before and after a run.

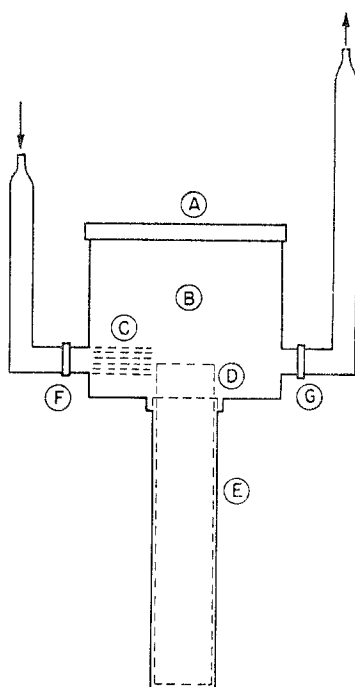


Figure 2. Diffusion Unit

- A. Cover
- B. Gas chamber
- C. Straightening vanes
- D. Diffusion tube
- E. Diffusion tube holder
- F, G. Union joint

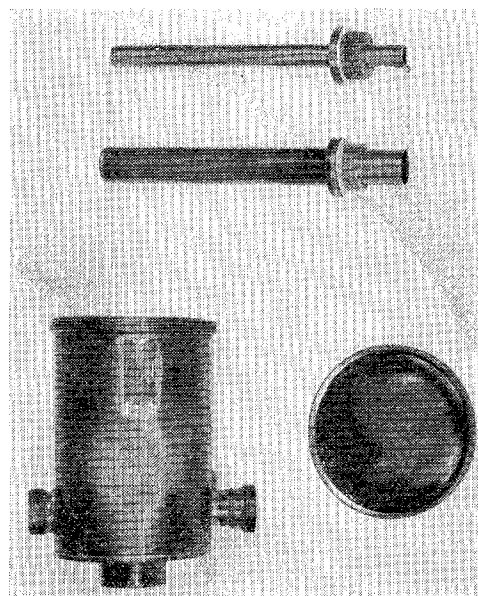


Figure 3. Diffusion Tube Assembly

When the diffusing vapor was lighter than the gas component—for example, water vapor and Freon 12—the diffusion tube was filled to a desired level with cotton saturated with the liquid. A disk of blotting paper of proper size was placed on top of the cotton to provide a smooth surface. After the tube had been placed in the holder, the whole diffusion unit was turned upside down and the run conducted as described above.

When air was used, the procedure was similar, except that the air was supplied directly from the room and was discharged into the room again after it swept over the diffusion tube. The con-

densing unit was disconnected in this case, but the air was dried with calcium chloride before it entered the apparatus. The water content of the outcoming air was measured at various times and utilized in the subsequent calculations.

For experiments using gases other than air, the purity of the gas in the system was measured by determining oxygen at the end of each run. In all cases contamination of the gas by air was less than 1% at the end of the run, making the average air content of the gas always 0.5% or less.

#### EVALUATION OF METHOD

Before the final procedure was adopted, several effects which might cause experimental error were investigated.

##### TEMPERATURE OF LIQUID SURFACE.

Latent heat must be supplied to the gas-liquid interface as vaporization proceeds. Heat is supplied mainly through the metal walls of the diffusion tube from the surrounding bath into the liquid and then through the liquid into the interface. As the temperature is lowered in the interface, free convection is induced. There is an additional contribution to the heat transfer process by conduction through the gas phase.

To explore the magnitude of temperature lowering in the interface, a tube 1.75 cm. in diameter and 17 cm. long was constructed with thermocouples of thin copper-advance wire placed in the center of the tube at distances of 4.6, 5.0, and 5.4 cm. from the open end. The tube was filled with liquid to a depth sufficient to immerse all the thermocouples, and placed in the apparatus in the manner described. The thermocouples were read at various time intervals as evaporation into air circulated over the tube caused the liquid surface to recede below each couple in turn. From the rate of evaporation the time required for the interface to coincide with each thermocouple could be calculated.

Because of their high vapor pressures and resulting rapid rates of vaporization, benzene, acetone, and ethyl ether were selected in addition to water for study in this manner. Table I gives the average lowering of interfacial temperature based on several determinations on each liquid, along with rates of vaporization and over-all average heat transfer coefficients between the interface and the surrounding bath. The heat transfer coefficients are larger than might be expected for free convection between liquids and plane solid surfaces. However, conditions for heat transfer may be more favorable in the present case where the liquid is bounded by gas. Interfacial temperature lowering was negligible in the experiments with water, which possesses a relatively high thermal conductivity and other properties favorable for heat transfer.

It is believed that these results indicate the order of magnitude effect which might be expected in an apparatus of this type, and that the interfacial temperature may be assumed equal to the bath temperature for most liquids, with negligible error in the resulting diffusion coefficient. By use of two or more diffusion path lengths in the measurements and extrapolation to infinite path length as described below, any error resulting from this assumption is greatly reduced. Therefore, in subsequent phases of the present work the liquid was assumed to vaporize at the temperature of the bath surrounding the diffusion tube.

**REVERSED THERMAL DIFFUSION EFFECT.** A temperature change associated with the spontaneous mixing of dissimilar

molecules was observed by Clusius and Waldman (3). This behavior represents a reversal of the phenomenon of thermal diffusion. In the present experiments, described above, the effect was evidenced by lower temperatures at the thermocouples 0.4 and 0.8 cm. above the interface than that indicated by the thermocouple at the liquid surface or by the thermometer at the upper end of the diffusion tube. Typical data are given in the right-hand column of Table I. For even the most extreme system studied, ethyl ether, the effect was not significantly large, never exceeding 0.1° C. By means of equations developed by Waldmann (22-24) the temperature 0.4 cm. above the liquid was calculated for the present case of ether vaporization and found to agree with the measured values within the accuracy of the experiment.

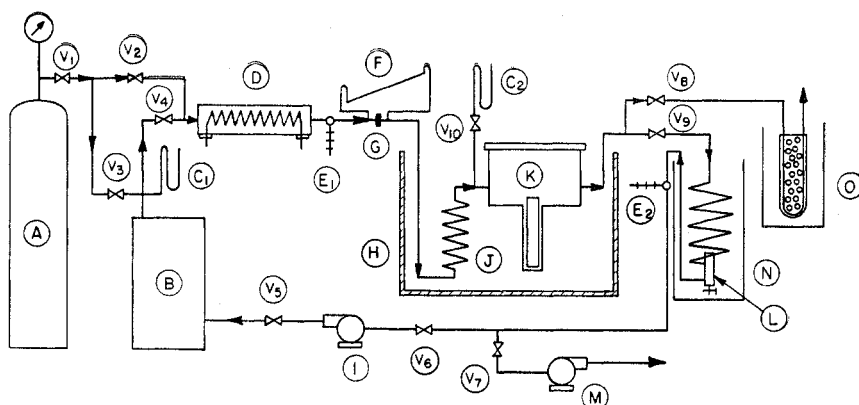


Figure 4. Flow Diagram of Apparatus

A. Gas cylinder  
B. Gas tank  
C<sub>1</sub>, C<sub>2</sub>. Pressure manometer  
D. Electric heater  
E<sub>1</sub>, E<sub>2</sub>. Thermometer  
F. Draft gage  
G. Orifice meter  
H. Thermostat

I. Gas blower  
J. Heating coil  
K. Diffusion unit  
L. Condensate receiver  
M. Vacuum pump  
N. Condensing unit  
O. Condensing unit  
V<sub>1</sub>-V<sub>10</sub>. Valves

**ESTABLISHMENT OF STEADY STATE.** It is of interest to determine the time required to establish conditions sufficiently close to the steady state so that Equation 1 may be used with negligible error. Although a rigorous solution of this problem would be extremely complicated, an approximate result may be obtained.

Assume the gas in the diffusion tube (Figure 1, a) to be initially saturated with vapor at partial pressure  $p_s$ . Assume further that  $p_s$  is so small that the diffusion process may be represented satisfactorily by Fick's second law:

$$\frac{\partial p}{\partial \theta} = D \frac{\partial^2 p}{\partial x^2} \quad (4)$$

TABLE I. COOLING EFFECT IN DIFFUSION

Diffusing Vapor	Vaporization Rate, G. Mole/Hr.-Sq. Cm.	Av. <sup>a</sup> Lowering of Interfacial Temp., ° C.	Av. Heat Transfer Coefficient, Bulk Liquid to Interface, B.t.u./Hr., ° F., Sq. Ft.	Temp. Change by Mixing, ° C.
Ether	$3.7 \times 10^{-3}$	$0.17 \pm 0.02$	300	0.10
Acetone	$1.38 \times 10^{-3}$	$0.10 \pm 0.02$	200	0.05
Benzene	$0.44 \times 10^{-3}$	$0.07 \pm 0.02$	100	0.05
Water	$0.30 \times 10^{-3}$	Undetectable	...	...

<sup>a</sup>  $T_b$ . Temperature of bath.  $T_s$ . Temperature of liquid surface, 5 cm. from mouth of tube.  $T_g$ . Temperature of gas 0.4 cm. above liquid. All experiments at 25° C., atmospheric pressure.

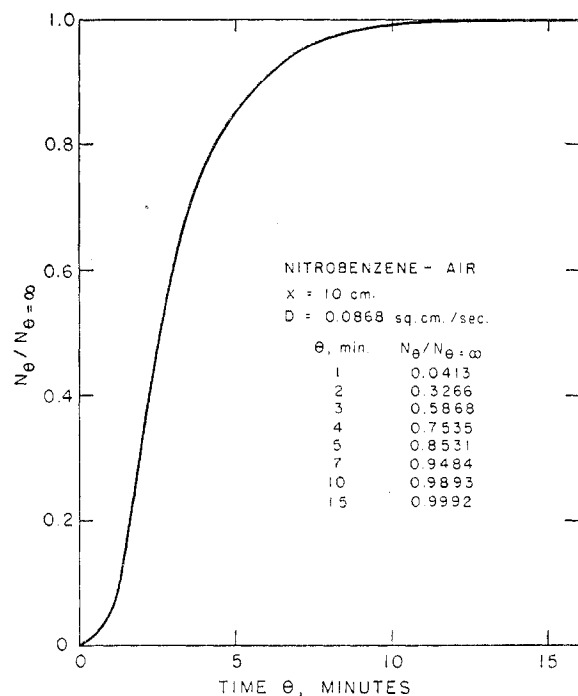


Figure 5. Time to Reach Steady State

It is convenient to define a variable,  $c = \frac{p}{p_s}$ , so that Equation 4 becomes

$$\frac{\partial c}{\partial \theta} = D \frac{\partial^2 c}{\partial x^2} \quad (5)$$

This equation must satisfy the boundary conditions:

$$\begin{aligned} c &= 1 \text{ at } x = x_0 \text{ for all } \theta \\ c &= 1 \text{ at } \theta = 0 \text{ for all } x \\ c &= 0 \text{ at } x = 0 \text{ for all } \theta > 0 \end{aligned}$$

Integration of Equation 5 is presented by Carslaw (2) for the analogous problem of heat conduction, and may be written for diffusion as follows:

$$c = \frac{x}{x_0} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\cos n\pi}{n} \times \sin \left( \frac{n\pi x}{x_0} \right) \times e^{-\frac{Dn^2\pi^2\theta}{x_0^2}} + \frac{2}{x_0} \sum_{n=1}^{\infty} \sin \frac{n\pi x}{x_0} e^{-\frac{Dn^2\pi^2\theta}{x_0^2}} \int_0^{x_0} \sin \frac{n\pi x}{x_0} dx \quad (6)$$

The ratio of the rate of evaporation at any time  $\theta$  to the rate at  $\theta = \infty$ —i.e., the steady state—is given by:

$$\frac{(N_A)_{\theta=\theta}}{(N_A)_{\theta=\infty}} = \frac{\left( \frac{\partial c}{\partial x} \right)_{x=x_0, \theta=\theta}}{\left( \frac{\partial c}{\partial x} \right)_{x=x_0, \theta=\infty}} \quad (7)$$

By differentiating Equation 6 with respect to  $x$  and setting  $x = x_0$ , the right hand member of Equation 7 may be evaluated to give the expression

$$\frac{(N_A)_{\theta=\theta}}{(N_A)_{\theta=\infty}} = 1 - 2e^{-\frac{D\pi^2\theta}{x_0^2}} + 2e^{-\frac{4D\pi^2\theta}{x_0^2}} - 2e^{-\frac{9D\pi^2\theta}{x_0^2}} + 2e^{-\frac{16D\pi^2\theta}{x_0^2}} - 2e^{-\frac{25D\pi^2\theta}{x_0^2}} \quad (8)$$

$x_0$  is assumed to remain constant over the time interval of interest.

Figure 5 shows the result obtained in the application of Equation 8 to the case of diffusion of nitrobenzene vapor into air in a tube with  $x_0 = 10$  cm., and  $D = 0.0868$  sq. cm. per second. This corresponds to the system in the present experiments requiring the longest time to approach steady state. The vaporization rate reaches 99.92% of the steady state rate in 15 minutes. It may therefore be concluded that for the present measurements, usually of 10 hours or more duration, the assumption of steady-state diffusion was satisfactory.

In the experiments with helium and Freon 12 the system was flushed with vapor-free gas for 10 minutes prior to starting circulation with the blower. Although the gas composition during this flushing period was slightly different than during the rest of the run, the error introduced by neglecting this difference was too small to justify correction.

**CORRECTION FOR END EFFECTS.** Because of surface tension forces the liquid surface in the tube will be curved, generally concave downward, and therefore the effective length of diffusion path will be somewhat shorter than that which would be measured at the center line of the tube or calculated from the volume of liquid in the tube.

As gas flows across the open end of the tube, any development of turbulence or eddies will increase the rate of diffusion through the space in the vicinity of the end. This may be viewed as extending the region of vapor-free gas (or unaltered gas composition) down into the tube and thereby reducing the effective diffusion path length.

By studying a given system at the same experimental conditions with two or more different lengths of diffusion path, the above end effects may be evaluated.

Assume the effective average diffusion path (Figure 1,b) in any experiment to be given by:

$$x = x_a - \Delta x_s - \Delta x_e = x_a - \Delta x \quad (9)$$

Then the rate of evaporation may be expressed by the equations:

$$N_A = \frac{D_a P \Delta p}{RT p_f x_a} = \frac{DP \Delta p}{RT p_f (x_a - \Delta x)} \quad (10)$$

where  $D_a$  = apparent diffusion coefficient, based on apparent diffusion path,  $x_a$

$D$  = true diffusion coefficient, based on effective diffusion path,  $x$

Equating the middle and right-hand members of Equation 10 gives:

$$\frac{1}{D_a} = \frac{-\Delta x}{D} \times \frac{1}{x_a} + \frac{1}{D} \quad (11)$$

Equation 11 indicates that a plot of  $\frac{1}{D_a}$  vs.  $\frac{1}{x_a}$  for various lengths of apparent diffusion path should be a straight line. From the intercept of the line extrapolated to  $\frac{1}{x_a} = 0$  the true diffusion constant may be evaluated.  $\Delta x$  may then be calculated from the slope of the line.

The result given by Equation 11 differs from the procedure of plotting  $D_a$  against  $1/x_a$  and extrapolating to zero as employed by Trautz and Müller (20). For sufficiently long diffusion paths, however, either method should be satisfactory, and this was usually the case in the systems Trautz and Müller studied.

Alternative to the graphical procedure, Equation 11 may be solved by a least squares treatment to give  $D$  by solution of the following simultaneous equations:

$$D \sum \frac{x_a}{D_a} - n \Delta x - \sum x_a = 0 \quad (12)$$

$$D \sum \left( \frac{x_a}{D_a} \right)^2 - \Delta x \sum \frac{x_a}{D_a} - \sum \frac{x_a^2}{D_a} = 0 \quad (13)$$

where  $n$  = number of measurements with corresponding apparent diffusion paths,  $x_a$ , and apparent diffusion constants,  $D_a$ .

TABLE II. SUMMARY OF EXPERIMENTAL RESULTS

Expt.	Q	$x_a$	P	$p_s$	$p_0$	$t_0$	Air, % <sup>a</sup>	$D_a$ <sup>b</sup>
Air-Water								
1	0.2	6.0	754	23.76	0.05	...	...	0.322
2	0.2	4.0	759	23.76	0.05	...	...	0.362
3	0.2	7.4	753	23.76	0.05	...	...	0.307
4	0.2	5.5	821	23.76	0.05	...	...	0.328
5	0.2	6.0	820	23.76	0.00	-170	...	0.321
6 <sup>c</sup>	0.2	5.07	758	23.76	0.00	-170	...	0.360
7 <sup>c</sup>	0.2	8.02	759	23.76	0.05	...	...	0.319
8 <sup>c</sup>	0.2	7.4	754	23.76	0.05	...	...	0.312
9 <sup>c</sup>	0.2	4.55	754	23.76	0.05	...	...	0.347
10 <sup>c,d</sup>	0.2	4.07	759	23.76	0.05	...	...	0.333
11 <sup>c,d</sup>	0.2	8.02	759	23.76	0.05	...	...	0.295
Air-Nitrobenzene								
12	0.17	6.02	748	0.291	0.00	...	...	0.1119
13	0.17	5.92	752	0.291	0.00	...	...	0.115
14	0.17	5.95	752	0.291	0.00	...	...	0.1098
15	0.17	8.00	748	0.291	0.00	...	...	0.1042
16	0.17	10.01	759	0.291	0.00	...	...	0.0997
17	0.13	7.87	759	0.291	0.00	...	...	0.0910
18	0.13	5.99	760	0.291	0.00	...	...	0.0930
Air-Benzene								
19	0.15	12.2	758	96.5	0.00	...	...	0.0971
20	0.15	4.18	758	96.5	0.00	...	...	0.0980
21	0.15	4.63	759	96.5	0.00	...	...	0.0977
22	0.15	4.58	749	96.5	0.00	...	...	0.0982
23	0.15	9.25	759	96.5	0.00	...	...	0.0972
24	0.15	4.20	759	96.5	0.00	...	...	0.0980
25	0.15	6.93	755	96.5	0.00	...	...	0.0971
26	0.20	5.32	756	96.5	0.00	...	...	0.1085
27	0.20	10.25	751	96.5	0.00	...	...	0.1028
28	0.20	10.65	752	96.5	0.00	...	...	0.1025
29	0.20	6.29	759	96.5	0.00	...	...	0.1062
Air-Ethyl Alcohol								
30	0.15	8.08	755	59.02	0.00	...	...	0.148
31	0.15	6.09	754	59.02	0.00	...	...	0.153
32	0.15	4.08	754	59.02	0.00	...	...	0.162
33	0.12	8.00	753	59.02	0.00	...	...	0.136
34	0.12	4.00	759	59.02	0.00	...	...	0.137
35	0.12	4.11	756	59.02	0.00	...	...	0.138
Helium-Benzene								
36	0.12	8.05	778	96.5	4.5	-22	...	0.384
37	0.12	4.08	778	96.5	4.5	-22	...	0.391
38	0.12	5.14	779	96.5	4.5	-22	0.8	0.387
Helium-Ethyl Alcohol								
39	0.12	4.05	780	59.02	2.1	-22	...	0.497
40	0.12	6.04	780	59.02	2.1	-22	...	0.495
41	0.12	8.03	779	59.02	2.1	-22	0.7	0.494
Helium-Nitrobenzene								
42	0.12	4.0	785	0.291	0.005 <sup>e</sup>	-22	...	0.408
43	0.12	4.0	784	0.291	0.005 <sup>e</sup>	-22	...	0.395
44	0.12	6.0	785	0.291	0.005 <sup>e</sup>	-22	0.8	0.390
Helium-Water								
45	0.10	7.22	777	23.76	0.6 <sup>e</sup>	-22	...	0.941
46	0.10	6.02	778	23.76	0.6 <sup>e</sup>	-22	...	0.942
47	0.10	5.01	779	23.76	0.6 <sup>e</sup>	-22	...	0.961
48	0.10	4.03	780	23.76	0.6 <sup>e</sup>	-22	0.7	0.973
Freon-Benzene								
49	0.14	4.0	831	96.5	32.5	4.0	...	0.0460
50	0.14	6.0	838	96.5	32.5	4.0	...	0.0430
51	0.14	6.0	831	96.5	32.5	4.0	0.6	0.0433
Freon-Ethyl Alcohol								
52	0.10	4.0	830	59.02	15.9	4.0	...	0.0490
53	0.10	6.2	831	59.02	15.9	4.0	...	0.0484
54	0.10	9.1	830	59.02	15.9	4.0	0.7	0.0480
Freon-Water								
55	0.13	4.1	831	23.76	6.10	4.0	...	0.151
56	0.13	6.0	831	23.76	6.10	4.0	...	0.135
57	0.13	4.9	829	23.76	6.10	4.0	...	0.144
58	0.13	8.0	828	23.76	6.10	4.0	0.6	0.125

<sup>a</sup> At end of running period on system.<sup>b</sup> At 760 mm., 25° C.<sup>c</sup> Upward diffusion.<sup>d</sup> 0.94-cm. tube diameter.<sup>e</sup> Estimated value.

## RESULTS

Apparent diffusion coefficients, adjusted to 760-mm. pressure, and other pertinent data for all the systems, are given for a range of apparent diffusion path lengths in Table II. Also presented are values of true diffusion coefficients based upon these measurements, summarized in Table III. Diffusion occurred at 25° C.

TABLE III. FINAL RESULTS FOR SYSTEMS<sup>a</sup>

System	D, Sq. Cm./Sec.
Air-benzene	0.0962
Air-ethyl alcohol	0.135
Air-nitrobenzene	0.0855
Air-water	0.260
Freon 12-benzene	0.0385
Freon 12-ethyl alcohol	0.0475
Freon 12-water	0.105
Helium-benzene	0.384
Helium-ethyl alcohol	0.494
Helium-nitrobenzene	0.372
Helium-water	0.908

<sup>a</sup> Converted to 760 mm., 25° C.

in all cases. With the exception of the systems water-air, benzene-air, and nitrobenzene-air, true diffusion coefficients reported are based on the least squares calculation, Equations 12 and 13. This method gave satisfactory agreement with the graphical procedure. Correction for presence of a small amount of air was applied to systems using helium or Freon as the gas by means of equations previously presented (4, 26). Air was determined at the end of each series of runs, and was assumed to have accumulated continuously with time in correcting the data. The resulting correction was so small that a more accurate procedure would have had little value.

Figures 6, 7, and 8 show the graphical application of Equation 11 to diffusion of water, benzene, and nitrobenzene in air to obtain extrapolated true diffusion coefficients and values of  $\Delta x$ . The agreement of the diffusion coefficient thus obtained for the water vapor-air system with previous data from the literature, and the convergence of lines for different flow rates in the nitrobenzene and benzene systems, are believed to indicate that the present method is fairly reliable. As shown on the figures,  $\Delta x$  increases markedly with increase in air rate, as would be expected in case of significant development of eddies at the mouth of the tube.

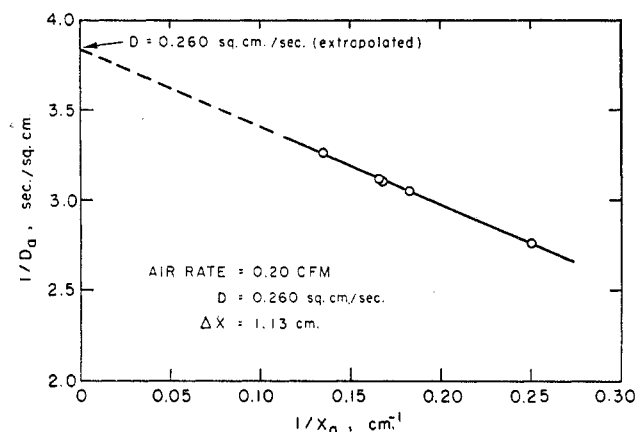


Figure 6. Diffusion of Water-Air

Attempts were made to separate  $\Delta x$  into components due to surface tension and air flow. Methods employed for this purpose involved elimination of the surface tension effect by vaporizing the liquid from a saturated cotton plug having a flat upper surface and attempting to find gas flow rates for which the effect of eddy formation was negligible. For the systems investigated with the diffusion tube 1.75 cm. in diameter,  $\Delta x$ , was estimated at 0.1 to 0.2 cm. and  $\Delta x_e$  ranged from essentially zero to 1.3 cm. No general correlation of these factors could be obtained. For vaporization of various liquids into the same gas,  $\Delta x_e$  appeared to be larger for systems of low vapor pressure. Existence of an interfacial resistance has been suggested as a possible factor in-

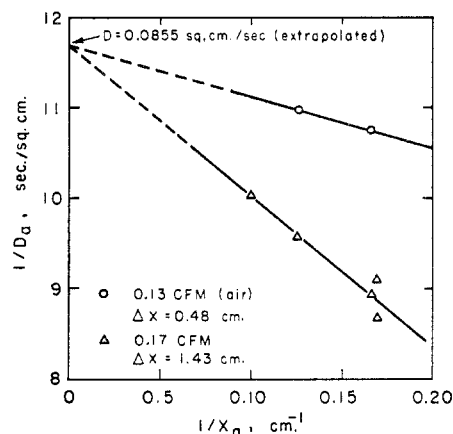


Figure 7. Diffusion of Nitrobenzene-Air

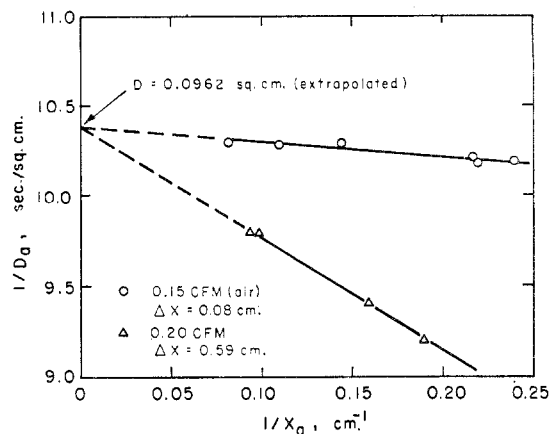


Figure 8. Diffusion of Benzene-Air

fluencing the apparent values of  $\Delta x_e$  (15). Further study would appear necessary to explain the observed behavior and to develop relations for predicting the magnitude of these effects.

#### DISCUSSION

In order to establish the accuracy of the present method, the result of the water-air system was compared with the available data. For purpose of comparison, all values were corrected to 25° C. and 760 mm. by determining the temperature coefficient if the data were reported at more than one temperature, or by calculating the temperature correction from the equations of Hirschfelder, Bird, and Spotz (6) if the data were reported at one temperature only. These results are summarized in Table IV. Data by Ackermann, Houdaille, and Summerhays have been omitted in computing the average of values in Table IV because they seemed obviously in error. The study by Schirmer is of particular interest for its coverage of temperatures up to near the boiling point. Failure to evaluate end effects may cause Schirmer's results to be slightly high, even though relatively long diffusion tubes were used. Kilbanora, Poerantsev, and Frank-Kammeritskii (8) have reported data over the range 373° to

1373° K. Results of the seven studies agreeing most closely suggest the value 0.257 sq. cm. per second as the probable best average diffusion coefficient at 25° C. and 760 mm.

The result for water-air obtained in this work agrees very satisfactorily with the various results of other studies and is believed to indicate the general validity of the method. Use of short diffusion paths, as in this work, introduces greater possi-

bility for experimental error because of the great influence of the  $\Delta x$  correction. However, the attendant reduction in time required for the measurements may justify the procedure when utmost precision is not necessary.

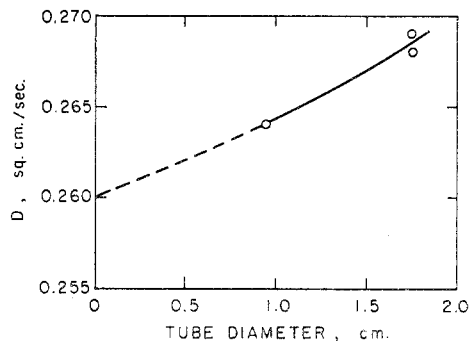


Figure 9. Upward Diffusion of Water Vapor into Air

Diffusion coefficients for water-air used as a basis for the values reported in Table III were obtained by downward diffusion from saturated cotton, as previously described. Additional experiments were made for upward diffusion with tubes 1.75 and 0.94 cm. in diameter to evaluate the extent to which mass transfer by free convection might affect the results. These data are shown graphically in Figure 9. A possible error of about 4% is indicated with the tube of large diameter. However, for upward diffusion of water vapor into Freon, a system with density differences more favorable to development of free convection, very large errors were obtained with the 1.75-cm. tube. It is therefore recommended that downward diffusion be used wherever the vapor is lighter than the gas. Alternatively, as suggested by Figure 9, several tube diameters might be used to permit extrapolation to zero tube diameter where free convection could not occur, although the correct method of extrapolation has not been established.

In view of the relatively large end-effect corrections required in the present experiments the data cannot be regarded as highly precise. However, the values are believed sufficiently accurate to be useful as a source of data for possible engineering applications involving diffusion of these substances.

#### NOMENCLATURE

$c$  =  $p/p_s$   
 $D$  = diffusion coefficient, sq. cm. per second  
 $D_a$  = apparent diffusion coefficient, sq. cm. per second  
 $M_A$  = molecular weight of diffusing vapor

TABLE IV. COMPARISON OF DATA ON WATER-AIR SYSTEM

Investigator	Reported Values		
	$T$ , ° C.	$D$ , Sq. cm./sec. at 760 mm.	$D$ at 25° C., 760 mm.
Guglielmo (10)	8	0.239	
	15	0.246	0.257
	18	0.248	
Houdaille (10)		0.203	0.242
Summerhays (11, 19)	16.1	0.282	0.317
LeBlanc and Wuppermann (12)	42	0.288	0.258
	67	0.336	...
Trautz (20)	16.6	0.244	...
	99.2	0.377	...
Gilliland (5)	25.9	0.258	0.257
Kimpton and Wall (9)	24.8	0.257	0.257
Winkelmann (27)	$D = 0.224 \left( \frac{T}{273} \right)^{1.774}$		0.261
Mache (18)	$D = 0.217 \left( \frac{T}{273} \right)^{1.89}$		0.256
Ackermann (1)	$D = 0.214 \left( \frac{T}{273} \right)^{2.87}$		0.275
Schirmer (16)	$D = 0.230 \left( \frac{T}{273} \right)^{1.81}$		0.269
Average of above results <sup>a</sup>			0.257
This work			0.260

<sup>a</sup> Excluding Houdaille, Schirmer, Summerhays, and Ackermann.

$N_A$  = vaporization rate, gram mole per sq. cm. per second  
 $N_\theta$  = vaporization rate at time  $\theta$ , gram mole per sq. cm. per second  
 $p$  = partial pressure of diffusing vapor  
 $p_f$  = log mean partial pressure of nondiffusing gas  
 $p_0$  = partial pressure of vapor in the circulating gas, mm. Hg or atmospheres  
 $p_s$  = liquid vapor pressure at the surface temperature, mm. Hg or atmospheres  
 $P$  = total pressure, mm. Hg or atmospheres  
 $Q$  = gas circulation rate, cu. feet per minute  
 $R$  = gas constant, cc. (atmosphere)(grams mole) $^\circ$  K.)  
 $S$  = cross section of diffusion tube, sq. cm.  
 $t_c$  = temperature of gas leaving condenser,  $^\circ$  C.  
 $T$  = temperature,  $^\circ$  K.  
 $W_A$  = grams of liquid evaporated in time,  $\theta$   
 $x$  = effective diffusion path length, cm.  
 $x_a$  = apparent diffusion path length, cm.  
 $x_0$  = value of  $x$  at zero time  
 $x_\theta$  = value of  $x$  at time  $\theta$   
 $\Delta p$  =  $p_s - p_0$   
 $\Delta x_s$  = effective change in diffusion path length due to surface tension  
 $\Delta x_e$  = effective change in diffusion path length due to eddies or turbulence  
 $\Delta x$  =  $\Delta x_s + \Delta x_e$   
 $\theta$  = total diffusion time, seconds

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RECEIVED for review January 19, 1953.

ACCEPTED June 1, 1954.

# Vapor-Liquid Equilibria of Alpha-Pinene-Beta-Pinene System

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A NUMBER of workers have determined the boiling point of  $\alpha$ -pinene, several have worked with  $\beta$ -pinene, and some have worked with gum turpentine, which is primarily a mixture of these two compounds (1, 3, 7, 13, 17). However, there has been little work done on the system composed of prepared mixtures of these two compounds. Fugitt, Stallcup, and Hawkins (4) studied the vapor-liquid equilibrium of the system composed of these two pure compounds in the pressure range 15 to 80 mm. of mercury.

The present work comprises a study of the vapor-liquid equilibrium of this system over the pressure range 20 to 750 mm. of mercury and over the complete range of composition. The third paper in this series on the physical and thermodynamic properties of terpenes was recently published (8).

## EXPERIMENTAL

**MATERIALS.** The  $\alpha$ -pinene and the  $\beta$ -pinene were obtained by careful fractionation of commercially prepared  $\alpha$ -pinene and  $\beta$ -pinene. This fractionation was carried out in columns of the Lecky and Ewell type (12). These columns were approximately 2.5 meters long and 2.5 cm. in inside diameter. The columns were wound with Nichrome wire, and the entire assembly was enclosed in a large glass tube. The Nichrome wire winding was connected through a variable transformer which permitted control of the heat so that no flooding occurred in the column. The columns were fitted with a magnetically controlled head and were operated at a reflux ratio of slightly greater than 100 to 1.

The purity of the distillate was checked by means of refractive

index. When the refractive index reached the proper value ( $\alpha$ -pinene, 1.4634;  $\beta$ -pinene, 1.4768) and remained constant the distillate was collected for future use.

These materials were stored by sealing in large glass ampoules at atmospheric pressure after the oxygen had been carefully blown out with nitrogen. It was later found that this method was not satisfactory in the case of  $\beta$ -pinene. Consequently, the  $\beta$ -pinene was redistilled and sealed in large glass ampoules under nitrogen at approximately 10 mm. of mercury pressure after the pressure had been repeatedly pumped down to about 5 mm. and then raised to atmospheric with nitrogen.

The mixtures were prepared as needed by mixing measured volumes of the two pure compounds.

**APPARATUS.** After a careful study of the various methods and apparatus used for the study of vapor-liquid equilibria, the apparatus described by Jones, Schoenborn, and Colburn (11) was selected. (This apparatus is frequently referred to in the literature as the Colburn apparatus.) The apparatus was modified so that quantities of material as small as 40 ml. could be used. Also, the three-way stopcock and connecting tube from the open end of the U-tube to the flash vaporizer were omitted, and the condenser was raised several inches farther above the flash vaporizer. This last modification was necessitated by the fact that the condensed vapors stood higher in the open end of the U-tube during operation at low pressures. As a check on the data, the apparatus designed by Gillespie (5) was modified and used. The modifications included enclosing the tube from the pot to the separation chamber and the separation chamber itself in a vacuum jacket; insertion of a three-way stopcock in the liquid return line just below the separation chamber for removal of the liquid sample; and use of an external heater with a small spot heater enclosed