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Binary Gaseous Diffusion Coefficients. Air with Furan Derivatives

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Binary gaseous diffusion coefficients at 1-atm pressure of air with furan derivatives were measured at three different temperatures for each system: furan (15, 20, and 25 °C), tetrahydrofuran (34, 42, and 55 °C), furfural, tetrahydrofurfuryl alcohol, and furfuryl mercaptan (125, 139, and 151 °C). Measurements were made by the capillary tube method of Stefan–Winkelmann. Diffusion coefficients calculated by the Chen–Othmer and Slattery–Bird equations show deviations from experimental results that depend on the boiling point temperature of the furan compound.

Among transport properties, experimental data on diffusion coefficients are particularly scarce in spite of their importance for the design of separation processes. The largest volume of diffusion coefficient data in binary systems has been reported with air as one of the components; however, a review of the available compilations (*2–4*, *6*, *8*, *10*, *13*) shows that measured values for air–furan derivatives are very rare or nonexistent.

The increasing use of agricultural residues as a source of furfural, a raw material for many chemicals, has led us to study the diffusivities with air of the following compounds: furan, furfural, tetrahydrofuran, tetrahydrofurfuryl alcohol, and furfuryl mercaptan.

Experimental Section

The experimental procedure is based on the Stefan–Winkelmann evaporation capillary tube method and has been reported previously (*1*, *11*). Several modifications have been introduced in the former apparatus, mainly in the design of the diffusion cell and flow control and in the improvement of the thermostatic conditions. This leads to the ensurance that mass transfer during evaporation of the liquid in the vertical tube will take place by molecular diffusion alone. A flow diagram of the system used in this work is shown in Figure 1 and details of the diffusion cell are shown in Figure 2.

The evaporation tube of Pyrex glass (0.18 cm i.d. × 20 cm length) was filled with the organic compound to a height of 11 cm and immersed in an adiabatic still, similar to the Othmer type used to determine vapor–liquid equilibrium data. A constant temperature of the still was obtained by boiling an organic compound, the vapors being condensed and recirculated to the still. This system ensures high heat transfer coefficients to the diffusion cell and therefore constant temperature conditions. By changing the organic liquid in the still, we can obtain different temperatures. The temperature of the boiling liquid in the still was measured by means of a Fenwall thermocouple probe connected with a Knauer commercial unit and was kept within ±0.05 °C.

The gas (high purity and previously dried air) flows through a coiled stainless steel tube (0.4 cm o.d. × 150 cm long) where it is heated by the condensing vapors of the still. The gas reaches the temperature of the diffusion vapors, passes over the top of the diffusion tube at constant flow rate, and is allowed to vent into the atmosphere with the diffusion vapors. Temperature in the diffusion cell was measured by means of a mercury thermometer with a sensitivity of 0.1 °C.

Depths of the liquid interface in the evaporation tube were measured with a Ealing cathetometer (±0.001 cm) approximately every 30 min, according to the nature of the system. Runs lasted between 1 and 3 days and about ten data points were taken for every diffusion coefficient data.

Table I. Critical Constants and Parameters Used in Calculations of Vapor Pressures and Diffusion Coefficients

substance	T_c, K	P_c, atm	V_c, cm^3/g-mol	T_b, °C	ref
air	132.5	37.17	90.52		13
furan	487	52.5	218	31.36	13
tetrahydrofuran	541	51.2	224	67	13
furfural	656	48.6	268	161.7	*a*
tetrahydrofurfuryl alcohol	638	45.9	300	177.8	*a*
furfuryl mercaptan	658	46.1	305	155	*a*

[a] Estimated values for the critical constants.

The pressure in the system was measured by means of three manometers connected to the adiabatic still and the evaporation chamber. An electronic relay allows that variations in all the experiments remain below 2 mmH$_2$O.

All the solvents used were Fluka or Merck reagent grade and were distilled in a packed column of the Oldershaw type with automatic control of the reflux ratio.

The experimental technique was tested with the system air–toluene at 1 atm and 100 °C; deviations were not higher than 1% from the most recent results (*1*, *8*, *11*).

Results and Discussion

Measurements were performed at three temperatures, and from data on liquid level, temperature, time, and vapor pressure of the pure compounds, the diffusion coefficient was determined by eq 1 based on a quasi-steady-state analysis (*11*, *12*, *16*, *17*)

$$z_i = -2z_0 + D_{AB}K(t_i/z_i) \qquad (1)$$

where

$$K = -\frac{2PM_A}{RT\rho_A}\ln\left(1 - \frac{p_A}{P}\right) \qquad (2)$$

Diffusion coefficients, D_{AB}, were obtained by adjusting data of t_i/a_i vs. z_i by the least-squares method determining the slopes for each datum point.

Vapor pressures of pure compounds were obtained from a Clapeyron equation and parameters reported in the literature (*15*) for furfural and from the Kirchhoff equation (*13*) for the other compounds. Critical constants were estimated by the Riedel (*13*) and Lydersen (*9*) correlations, when experimental data were not available. A summary of the critical constants and parameters used is shown in Table I.

The experiments were conducted so that initially the liquid meniscus was quite close to the air nozzle, which sweeps across the top of the capillary tube. Hence the early time experiments are somewhat error prone owing to turbulence at the top of the capillary (*3*, *12*). These data were ignored in the subsequent analysis of results.

Moreover, the experimentation times used were somewhat shorter when compared to similar systems (*11*), in order to prevent any possible oxidation of the liquid.

The experimental diffusion coefficients at various temperatures are given in Table II and also calculated values from Chen–Othmer (*5*) and Slattery–Bird (*14*) equations.

Calculated and experimental diffusion coefficients are in fairly good agreement for the system air–tetrahydrofuran. For those

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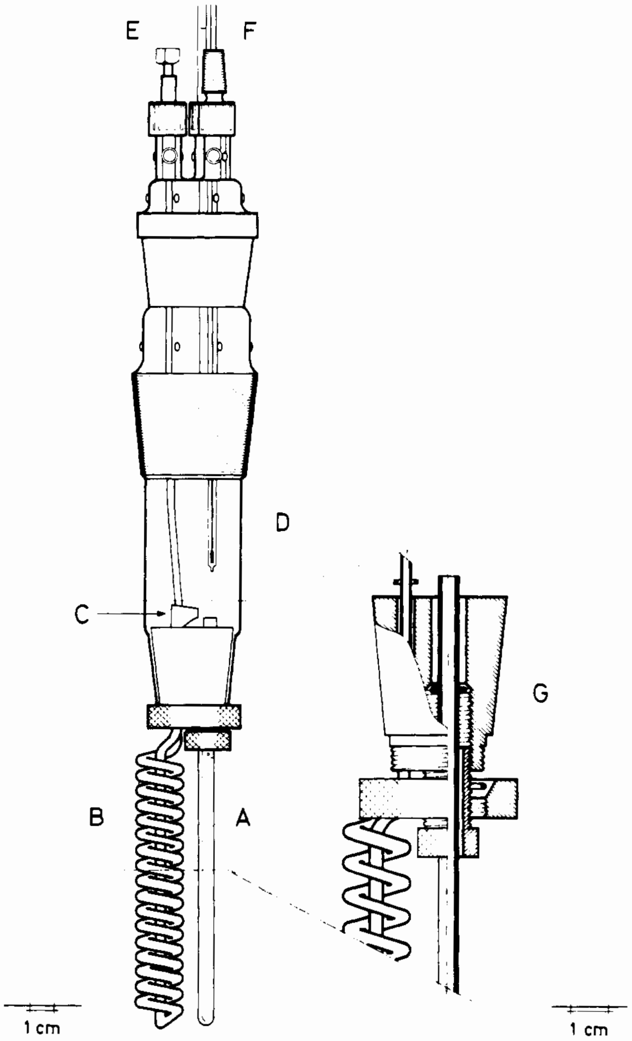

Figure 1. Details of the diffusion chamber: A, evaporation capillary tube with reference mark; B, coiled tubing for gas preheating; C, nozzle to direct the gas phosphoric the top of tube A; D, flow chamber; E, gas inlet; F, gas and diffusion vapors outlet; G, section view of the preheater and evaporation tube assembly.

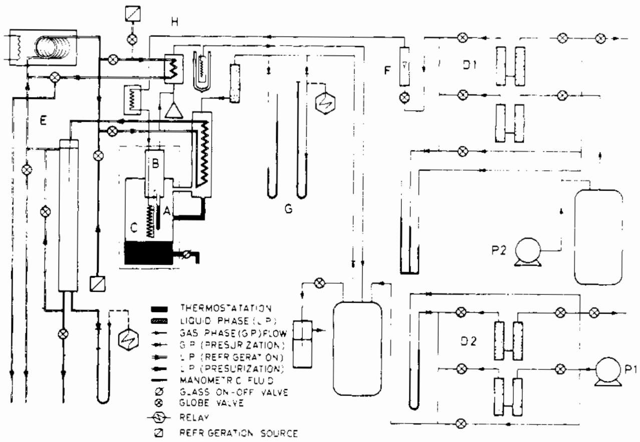

Figure 2. Flow diagram of the experimental technique: A, evaporation capillary tube; B, diffusion chamber; C, adiabatic still; D1, D2, drying tubes containing silica gel and phosphoric acid; E, closed and open refrigeration circuit; F, rotameter; G, system for measuring and control of the diffusion chamber pressure; H, traps for collection of vented vapors; P1, P2, pressurization and gas flow pumps.

Table II. Experimental and Calculated Diffusion Coefficients D_{AB} (cm^2 s^{-1}) for Air–Furan Derivatives at 760 mmHg

T, °C	D_{AB} exptl	D_{AB} calcd (*13*)	D_{AB} calcd (*14*)
	Air–Furan		
15	0.0997	0.0921	0.0957
20	0.1044	0.0950	0.0968
25	0.1107	0.0980	0.1021
	Air–Furfural		
125	0.1765	0.1373	0.1390
139	0.1778	0.1462	0.1460
151	0.1835	0.1540	0.1560
	Air–Tetrahydrofuran		
34	0.1058	0.0998	0.0984
42	0.1108	0.1045	0.1031
55	0.1200	0.1127	0.1138
	Air–Tetrahydrofurfuryl Alcohol		
125	0.1275	0.1295	0.1374
139	0.1316	0.1378	0.1463
151	0.1356	0.1452	0.1542
	Air–Furfuryl Mercaptan		
125	0.1189	0.1265	0.1340
139	0.1269	0.1347	0.1427
151	0.1409	0.1419	0.1504

systems in the series where the organic compound has a low boiling temperature, experimental results tend to be higher than the calculated ones. When the boiling temperature is high, calculated results are higher than those of experimental data, and in this case the Chen–Othmer equation generally gives better results. The air–furfural system shows the highest deviations between calculated and experimental results. However, a comparison between experimental and calculated data is not very reliable especially for those systems where the critical constants were estimated by the Riedel and Lydersen correlations.

Glossary

D_{AB}	molecular diffusion coefficient, cm^2 s^{-1}
K	constant for each system defined by eq 2, dimensionless
M	molecular weight
P	total pressure, atm
p_A	partial pressure at the interface, atm
P_c	critical pressure, atm
R	gas constant, atm cm^3 K^{-1} g-mol^{-1}
t	time, s
T	absolute temperature, K
T_b	boiling point temperature, °C
T_c	critical temperature, K
V_c	critical volume, cm^3 g-mol^{-1}
ρ	density, g cm^{-3}
z_0	initial interface depth, cm
z_l	drop of the interface depth, cm

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