Temperature Dependence of Gas and Vapor Diffusion Coefficients

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The dependence of diffusion coefficients on temperature has been determined over a 100 to 200 degree centigrade range for several gases and vapors. Using helium as one component values were determined using Ar, CO_2, N_2, O_2, benzene, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol and 1-hexanol as the other component. The new and rapid gas-chromatographic method, developed previously by the authors, was used. The parameter m in the T^m dependence of diffusivity had an average value of 1.70 for both the gases and vapors although individual variations from this were rather large. A comparision is made between the various methods for measuring the diffusion coefficients of vapors.

EXPERIMENTAL values have been obtained for the binary diffusion coefficients of gas-gas and gas-vapor mixtures over a range of temperatures up to 250° C. A least squares analysis has been used to obtain the exponent m in the assumed T^m dependence of the diffsuion coefficients. The results can be compared with various semi-theoretical expressions for temperature effects.

The experimental method involves the use of a gas chromatographic apparatus containing a long (~ 14 m) empty diffusion tube. The diffusion coefficient is obtained in terms of the dispersion of a narrow pulse of a trace component as it is moved through the column by the carrier gas. Because of a magnification effect, the pulse dispersion is greater than that resulting from purely longitudinal diffusion effects. A short correction tube is used to subtract the end effects, including those originating in the injection and detection devices. The vapor samples were obtained by injecting 0.1 μl. of liquid into the vaporization chamber with a Hamilton microliter syringe. This sample size is so small that diffusion proceeds, except for a short initial period, at sample concentration level which is effectively zero (*6*). A more complete description of the experimental technique and underlying theory has been presented earlier (*4-6*).

The method used in this work has the advantage of yielding diffusion coefficients in a very short time (the order of a few minutes each). In addition, the accuracy and reproducibility are good, only trace quantities are needed, and the apparatus, including accurate temperature controls, is available commercailly. Some commercial instruments permit temperatures as high as 500° C. to be reached. For even greater accuracy and speed, special instrumentation is needed. Work is now underway in this laboratory on an improved instrument system.

The method described above has not heretofore been applied to the measurement of gas-vapor diffusion coefficients. The advantages, however, would seem to be greater than those found in the application to gas-gas systems. With a sensitive detector it would be possible to range well above and below the boiling point of the mother liquid. The latter, particularly, is very time consuming when conventional techniques are employed.

Of the current methods used to measure vapor diffusion coefficients, that of Stefan (*12*) is considered the best and has been most widely used (*1, 3, 7-11, 17*). This method has several drawbacks. The precision is not good for the vapors of liquids which have very high or very low vapor pressures and the method is thus limited to a rather narrow temperature range (*7*). No measurements whatsoever can be made above the boiling temperature of the liquid. A relatively large quantity of liquid is needed for each diffusion coefficient determination. Finally, each measurement involves a waiting period of several hours average duration.

MATERIALS

Helium was used as the carrier gas in all the work reported here. The gases used as trace components were Ar, Co_2, N_2 and O_2. The vapors were benzene, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol, and 1-hexanol.

RESULTS

The results of the binary gaseous measurements are shown in Table I. The values have been converted to standard atmospheric pressure. Each diffusion coefficient was obtained as an average of six separate determinations. The indicated precision is the average deviation of individual measurements. A plot of the data in the form of ln D (diffsuion coefficient) ln T (absolute temperature) has been made in Figures 1 and 2 to evaluate the exponent m. A least squares analysis of each plot gave values for m as follows, with the indicated precision being that for

Table I. Effect of Temperature on the Diffusion Coefficient of Gases

Temp.,	D(Cm².Sec.)			
° C.	He–N_2	He–O_2	He–Ar	He–CO_2
225.0	1.650 ± .021	1.683 ± .018	1.728 ± .023	1.414 ± .028
200.0	1.569 ± .007	1.595 ± .026	1.612 ± .014	1.279 ± .019
170.0	1.289 ± .014	1.420 ± .008	1.401 ± .020	1.133 ± .018
140.0	1.200 ± .019	1.245 ± .014	1.237 ± .014	1.040 ± .011
110.0	1.077 ± .020	1.120 ± .016	1.122 ± .014	0.884 ± .008
80.0	0.893 ± .005	0.987 ± .003	0.978 ± .010	0.800 ± .013
50.0	0.766 ± .008	0.809 ± .007	0.809 ± .010	0.678 ± .012
25.0	0.687 ± .006	0.729 ± .010	0.729 ± .009	0.612 ± .003

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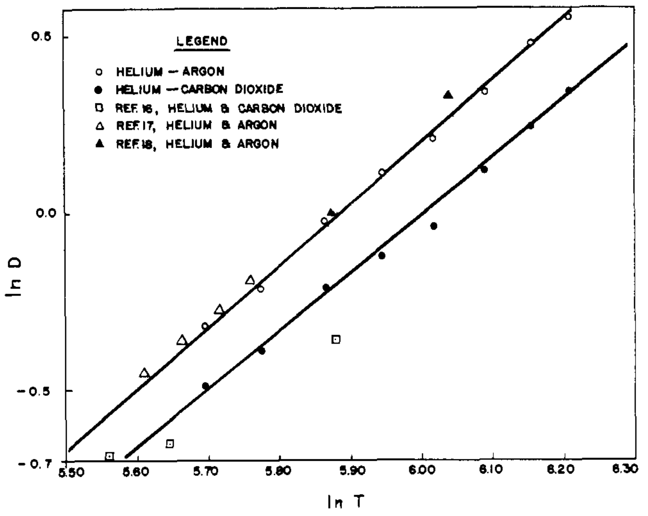

Figure 1. Temperature dependence of binary diffusion coefficients: He–Ar and He–CO_2

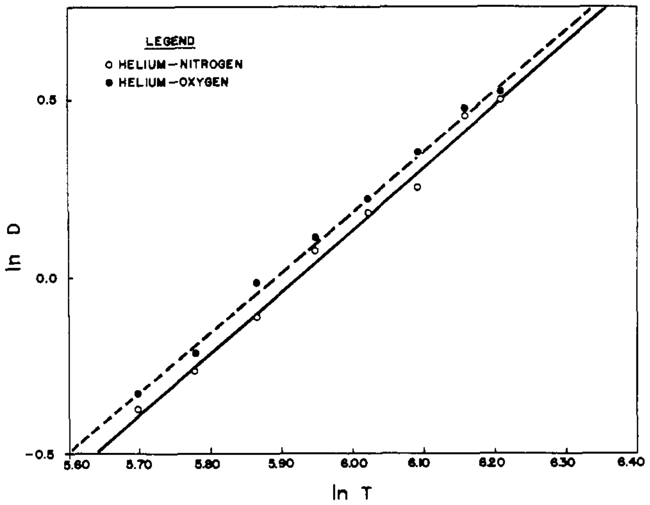

Figure 2. Temperature dependence of binary diffusion coefficients: He–N_2 and He–O_2

Table II. Effect of Temperature on Vapor Diffusion Coefficients

Temp., °C.	D(Cm²/Sec.)							
	Benzene	Methanol	Ethanol	1-Propanol	2-Propanol	1-Butanol	1-Pentanol	1-Hexanol
150.0	0.610±.002	1.032±.022	0.821±.009	0.676±.016	0.677±.022	0.587±.011	0.507±.005	0.469±.007
170.0	0.662±.001	1.135±.019	0.862±.010	0.711±.007	0.732±.005	0.653±.006	0.536±.004	0.496±.007
190.0	0.715±.003	1.218±.021	0.925±.015	0.761±.018	0.784±.006	0.689±.006	0.578±.013	0.531±.001
210.0	0.766±.012	1.335±.036	0.997±.031	0.829±.005	0.834±.011	0.746±.006	0.636±.007	0.584±.012
230.0	0.815±.012	1.389±.015	1.048±.005	0.896±.005	0.882±.006	0.792±.009	0.666±.005	0.631±.004
250.0	0.861±.001	1.475±.009	1.173±.004	0.959±.001	0.988±.020	0.841±.001	0.729±.007	0.686±.003

a 90% confidence limit: He–Ar, 1.73 ± 0.07; He–Co_2, 1.63 ± 0.07; He–N_2, 1.75 ± 0.12 and He–O_2, 1.70 ± 0.08.

The results of the vapor diffusion measurements are shown in Table II. The values have much the same meaning as do those of Table I (converted to standard pressure, etc.). A least squares plot (not shown) of ln D *vs.* ln T for each system yields the following results: benzene, 1.63 ± 0.07; methanol, 1.68 ± 0.18; ethanol, 1.64 ± 0.25; 1-propanol, 1.70 ± 0.17, 2-propanol, 1.69 ± 0.22; 1-butanol, 1.66 ± 0.14; 1-petanol, 1.73 ± 0.17; and 1-hexanol, 1.83 ± 0.20.

DISCUSSION

A comparison of the results obtained for He–Ar, and He–CO_2 with those of other investigators shows satisfactory agreement as demonstrated by Figure 1. The slightly lower values found here for the He–Ar system are not surprising in view of the difference in relative concentration used here and in the other studies. Such concentration differences can easily account for the observed difference of approximately 3% (*6*).

To compare the vapor diffusion coefficients with literature values, the logarithmic plots for benzene and ethanol were extrapolated to 25° C. and yielding 0.347 and 0.457 sq. cm./sec., respectively. The reported values are 0.384 and 0.494 (*9*). Since no significant difference exists in the present technique between the measurement of gas and vapor diffusion coefficients, it would be difficult to attribute the entire error to this method. Lee and Wilke (*9*), Trautz (*13*) and Gilliland (*7*) have discussed the errors associated with the Stefan method. All of these tend to make the experimental coefficient larger than its true value. Lee and Wilke, however, have apparently eliminated most of these errors from their work. A third method, perhaps the point source technique (*16*), might well be used to remove some of the uncertainty related to these measurements.

The exponent m shows a fair amount of deviation from one system to another, but much of this, especially for vapors, may be attributed to experimental error. The average for all gases yields m = 1.70 and the average for all vapors is also 1.70. The significance of m in relationship to the theories of diffsuion has been summarized by Chen and Othmer (*2*).

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