

CHAPTER V

RESULTS AND DISCUSSION

This chapter is organized into three sections. Section 5.1 gives the entire body of experimental data for diffusion, viscosity, and density and includes literature values for comparison wherever possible. In Section 5.2 the predictions from several available equations are compared to the experimental results. The physical basis for the hydrodynamic theory is shown to be incorrect when a wide temperature range is considered. In section 5.3 the data are analyzed in terms of the rough hard sphere kinetic theory. We first show that the behavior of the diffusion coefficient follows the predictions of RHS theory, which is remarkable considering the wide range of solute/solvent sizes and shapes which were investigated. Using our data, we then developed the first practical working equation for predicting diffusion coefficients at the elevated temperatures typical of most chemical processes. Finally, we discuss the applicability of this equation to other systems, including Fischer-Tropsch reactor wax.

5.1 Measured Values of Diffusion Coefficients, Viscosity, and Density

Mutual diffusion coefficients at infinite dilution for n-octane, n-decane, n-dodecane, n-tetradecane, and n-hexadecane in the alkane solvents n-heptane, n-dodecane, n-hexadecane are given in Table 5.1. The data cover the temperature range 298 to 566 K at pressures of approximately 1400 and 3450 kPa (about 200 and 500 psia). Diffusivities of hydrogen, carbon monoxide, and carbon dioxide are given in Table 5.2. Most entries in these tables represent the average of at least three repetitive measurements. The uncertainties in the tables are one standard deviation.

Table 5.1 Infinite Dilution Diffusion Coefficients for Alkanes
in n-Heptane, n-Dodecane, and n-Hexadecane
($D_{12} \times 10^9 \text{ m}^2/\text{s}$, ± 1 standard deviation)

T (K)	P (kPa)	C ₈	C ₁₀	C ₁₂	C ₁₄	C ₁₆
Solvent: n-Heptane						
298	101	2.82 ± 0.07	-	2.21 ± 0.08	1.92 ± 0.15	1.83 ± 0.04
374	3480	6.12 ± 0.14	5.45 ± 0.02	4.90 ± 0.04	4.45 ± 0.03	4.03 ± 0.02
427	710	-	8.93 ± 0.01	-	-	6.87 ± 0.01
427	3460	9.79 ± 0.09	8.69 ± 0.01	7.73 ± 0.03	6.87 ± 0.01	6.43 ± 0.01
476	1410	-	12.9 ± 0.2	-	-	10.8 ± 0.0
476	3480	15.3 ± 0.0	13.0 ± 0.0	11.9 ± 0.0	10.8 ± 0.0	10.1 ± 0.1
Solvent: n-Dodecane						
304	1410	1.27 ± 0.02	1.09 ± 0.04	-	0.83	-
373	1410	3.33 ± 0.02	2.95 ± 0.12	-	2.05 ± 0.16	1.96 ± 0.06
373	3440	3.49 ± 0.16	-	-	-	-
443	1450	6.79 ± 0.12	5.83 ± 0.06	-	4.26 ± 0.13	4.01 ± 0.03
443	3450	6.79 ± 0.20	-	-	-	-
513	1450	11.5 ± 0.01	9.71 ± 0.00	-	7.45 ± 0.40	7.04 ± 0.13
515	3430	11.2 ± 0.1	-	-	-	-
566	1460	17.3 ± 0.1	15.1 ± 0.2	-	12.2 ± 0.1	11.2 ± 0.1
566	3440	16.2 ± 0.1	-	-	-	-
Solvent: n-Hexadecane						
323	1420	1.19 ± 0.03	0.99 ± 0.02	0.95 ± 0.09	-	-
323	3459	1.25 ± 0.09	-	-	-	-
371	1402	2.31 ± 0.02	2.06 ± 0.03	-	-	-
371	3444	2.36 ± 0.02	-	-	-	-
443	1383	5.19 ± 0.08	4.35 ± 0.05	4.09 ± 0.11	-	-
443	3425	5.05 ± 0.07	-	-	-	-
514	1412	9.50 ± 0.44	-	7.08 ± 0.21	-	-
514	3427	9.10 ± 0.52	-	-	-	-
564	1404	13.1 ± 0.3	12.5 ± 0.7	10.4 ± 0.7	-	-
564	3408	12.7 ± 0.1	-	-	-	-

Table 5.2 Infinite Dilution Diffusion Coefficients for Gases
in n-Heptane, n-Dodecane, and n-Hexadecane
($D_{12} \times 10^9 \text{ m}^2/\text{sec}$, ± 1 standard deviation)

T (K)	P (kPa)	H ₂	CO	CO ₂
Solvent: n-Heptane				
298	101	20.9 ± 0.4	6.41 ± 0.30	-
427	3450	63.5 ± 0.3	24.1 ± 0.2	-
Solvent: n-Dodecane				
304	1390	10.7 ± 0.1	4.69 ± 0.12	3.84 ± 0.01
372	1410	25.8 ± 0.1	9.69 ± 0.11	8.61 ± 0.03
372	3440	24.0 ± 0.1	9.29 ± 0.03	8.60 ± 0.02
445	1450	45.5 ± 0.4	17.3 ± 0.1	15.8 ± 0.1
443	3450	41.6 ± 0.1	18.0 ± 0.3	15.9 ± 0.2
513	1450	76.7 ± 0.1	28.5 ± 0.1	25.6 ± 0.1
515	3440	72.2 ± 0.4	26.5 ± 0.5	25.1 ± 0.2
567	1460	114 ± 1.0	44.3 ± 0.3	37.8 ± 0.3
567	3440	109 ± 0.2	46.2 ± 1.6	35.8 ± 0.3
Solvent: n-Hexadecane				
323	1420	10.4 ± 0.1	4.39 ± 0.36	3.55 ± 0.01
323	3460	-	3.63 ± 0.07	3.47 ± 0.04
371	1400	19.4 ± 0.1	6.57 ± 0.15	6.52 ± 0.01
371	3440	18.5 ± 0.1	6.75 ± 0.13	6.39 ± 0.06
443	1400	34.5 ± 0.4	14.0 ± 0.1	12.6 ± 0.1
443	3430	35.7 ± 0.3	13.5 ± 0.2	12.3 ± 0.0
513	1410	55.8 ± 1.8	23.1 ± 0.4	20.5 ± 0.0
513	3430	56.1 ± 0.3	22.0 ± 0.2	20.2 ± 0.0
564	1400	79.3 ± 2.4	33.2 ± 0.4	28.3 ± 0.1
564	3410	72.4 ± 2.2	30.1 ± 0.4	27.6 ± 0.2

For the solvents n-heptane, n-dodecane, and n-hexadecane, we investigated the effect of moderate increases in pressure on the diffusion coefficient. For this reason, much of the data in Tables 5.1 and 5.2 is duplicated at both 1400 and 3450 kPa. The results show that over this pressure range there is a small negative effect of pressure on the diffusion coefficient, while the effect of temperature is much larger. An increase of pressure increases density, which decreases the free volume available for diffusion. Therefore, the diffusion coefficient is expected to decrease as pressure increases, a trend which is demonstrated in most of our data. Because the density changes with pressure are small (on the order of 1 to 2%) and because the resulting change in diffusivity is small, it is not possible to use this data to quantitatively extract the pressure dependence of the diffusion coefficient. We simply note that the observation is consistent with expectations, and that the magnitude of the effect is approximately the same for all solutes.

Table 5.3 includes the diffusion coefficients for the alkane solutes in the solvents n-eicosane, n-octacosane, and Fischer-Tropsch reactor wax. The data for these solvents was collected over the temperature range 375 to 536 K at approximately 1400 kPa (200 psi). Diffusion coefficients for the gaseous solutes hydrogen, carbon monoxide, and carbon dioxide were collected at approximately the same conditions and are reported in Table 5.4.

Figures 5.1 through 5.4 illustrate the effects of temperature, solute, and solvent characteristics on the infinite dilution diffusion coefficient. Data at approximately 200 psia were plotted for the solvents n-heptane, n-hexadecane, (C_{12}) and n-octacosane (C_{28}) to illustrate several trends which are typical of all the data.

For every solute-solvent system, the diffusion coefficient increases rapidly as temperature increases. At a constant temperature, the diffusion coefficient is larger

Table 5.3 Infinite Dilution Diffusion Coefficients for Alkanes
in n-Eicosane, n-Octacosane, and Fischer-Tropsch Wax
($D_{12} \times 10^9 \text{ m}^2/\text{s}$, ± 1 standard deviation)

T (K)	P (kPa)	C ₈	C ₁₀	C ₁₂	C ₁₄	C ₁₆
Solvent: n-Eicosane						
375	1380	1.85 \pm 0.06	-	1.33 \pm 0.01	-	1.06 \pm 0.03
413	1410	2.86 \pm 0.02	2.43 \pm 0.01	2.13 \pm 0.01	1.87 \pm 0.03	1.68 \pm 0.02
454	1400	4.22 \pm 0.01	-	3.19 \pm 0.01	-	2.56 \pm 0.02
495	1380	6.09 \pm 0.04	5.33 \pm 0.02	4.65 \pm 0.03	4.15 \pm 0.02	3.75 \pm 0.02
534	1320	8.34 \pm 0.00	-	6.36 \pm 0.06	-	5.08 \pm 0.26
Solvent: n-Octacosane						
373	1430	1.21 \pm 0.03	-	0.89 ¹	-	0.71 \pm 0.01
413	1380	2.16 \pm 0.01	-	1.56 \pm 0.05	-	1.25 \pm 0.01
454	1380	3.20 \pm 0.09	-	2.37 \pm 0.01	-	1.89 \pm 0.02
495	1390	4.70 \pm 0.07	-	3.59 \pm 0.04	-	2.84 \pm 0.10
534	1370	6.33 \pm 0.08	-	4.82 \pm 0.09	-	3.91 \pm 0.04
Solvent: Fischer-Tropsch Wax						
475	1400	3.99 \pm 0.07	-	2.88 \pm 0.11	-	1.88 \pm 0.12
504	1400	5.15 \pm 0.06	-	3.69 \pm 0.23	-	2.55 \pm 0.08
536	1400	6.07 \pm 1.15	-	4.86 \pm 0.08	-	3.02 \pm 0.13

1. This value represents a single measurement.

Table 5.4 Infinite Dilution Diffusion Coefficients for Gases
in n-Eicosane, n-Octacosane, and Fischer-Tropsch Wax
($D_{12} \times 10^9 \text{ m}^2/\text{sec}$, ± 1 standard deviation)

T (K)	P (kPa)	H ₂	CO	CO ₂
Solvent: n-Eicosane				
374	1340	16.6 ± 0.5	5.69 ± 0.06	5.21 ± 0.07
413	1400	23.9 ± 0.2	8.29 ± 0.16	7.71 ± 0.03
450	1370	33.0 ± 0.0	11.7 ± 0.4	10.5 ± 0.1
495	1420	46.6 ± 0.5	17.0 ± 0.2	15.1 ± 0.0
534	1410	-	22.4 ± 0.5	19.6 ± 0.2
Solvent: n-Octacosane				
371	1360	13.4 ± 0.0	4.36 ± 0.16	3.80 ± 0.07
414	1350	20.5 ± 0.3	6.98 ± 0.05	6.12 ± 0.20
455	1350	29.3 ± 0.3	10.7 ± 0.0	8.99 ± 0.20
496	1360	41.0^1	15.7 ± 0.5	12.7 ± 0.1
534	1340	51.5 ± 0.3	18.8 ± 0.2	15.5 ± 0.4
Solvent: Fischer-Tropsch Wax				
475	1400	36.9 ± 0.7	15.1^1	10.7 ± 0.7
504	1400	47.3 ± 1.7	17.4 ± 0.3	14.0 ± 0.3
536	1400	NA ²	21.7 ± 0.2	18.1 ± 0.7

1. This value represents a single measurement.

2. At this condition, hydrogen reacted with a component of the FT wax.

DIFFUSIVITY OF ALKANES IN N-HEPTANE
298 TO 476 K, 500 psia

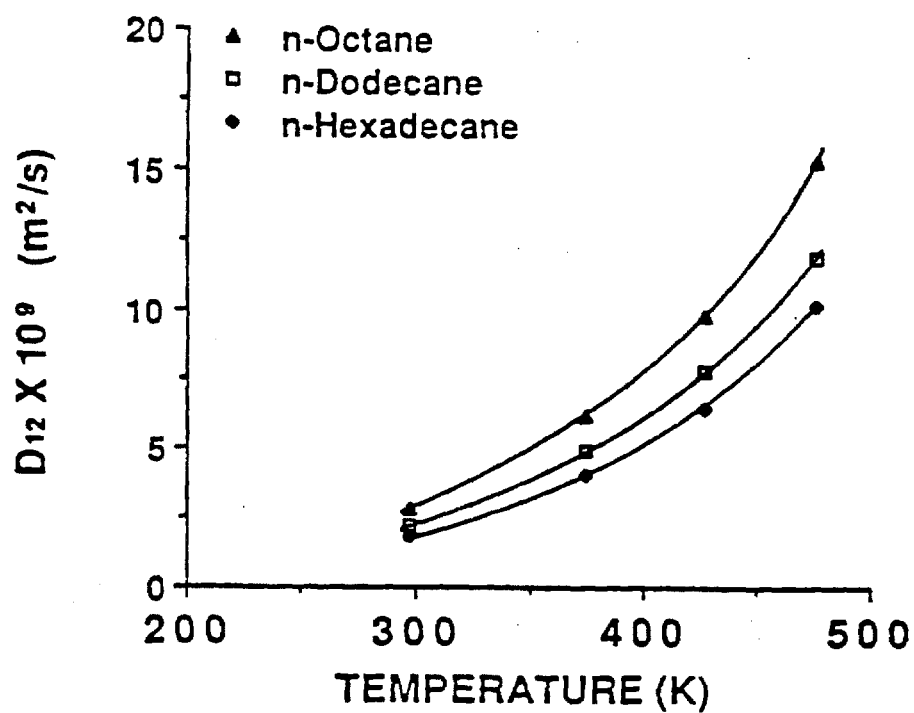


Figure 5.1. Diffusion coefficients for n-alkanes in n-heptane.

DIFFUSIVITY OF GASES IN N-HEXADECANE
323 TO 564 K, 200 psia

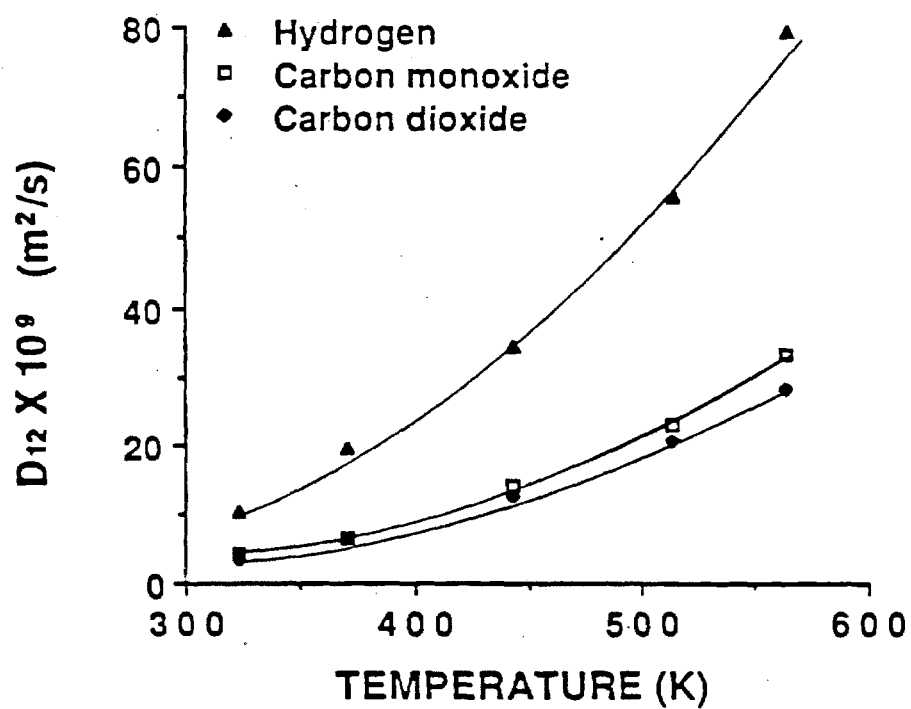


Figure 5.2. Diffusion coefficients for gases in n-hexadecane.

DIFFUSIVITY OF ALKANES IN N-OCTACOSANE
372 TO 535 K, 200 psia

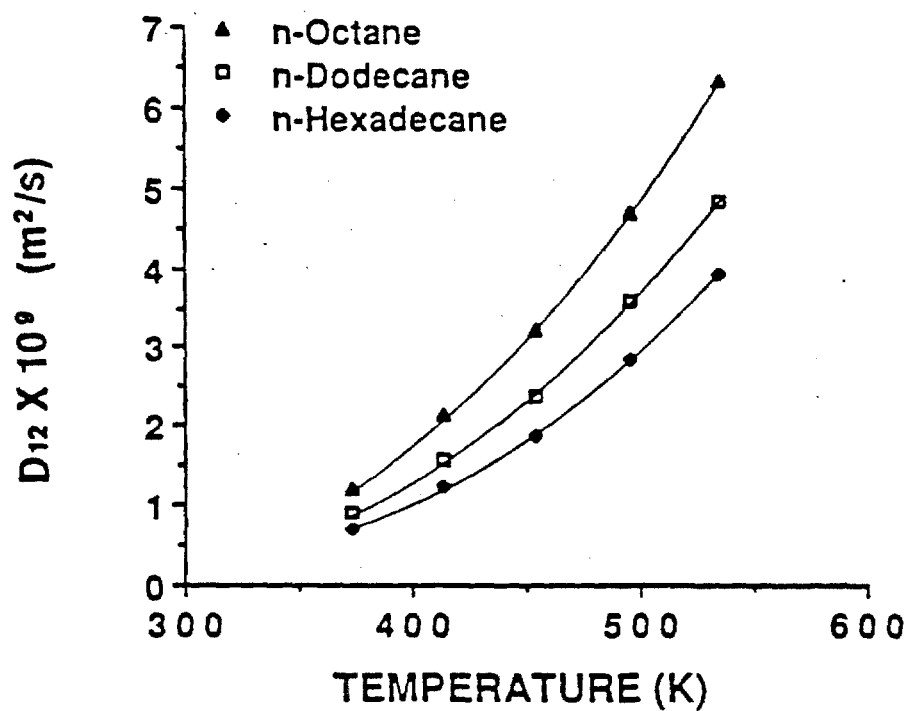


Figure 5.3. Diffusion coefficients for n-alkanes in n-octacosane.

DIFFUSIVITY OF GASES IN N-OCTACOSANE
371 TO 535 K, 200 psia

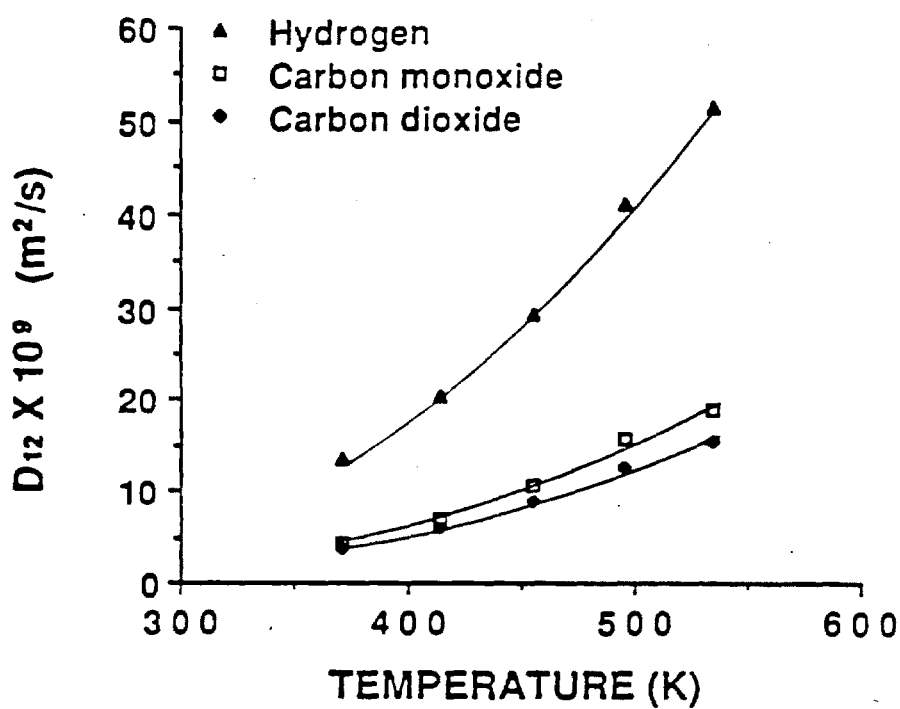


Figure 5.4. Diffusion coefficients for gases in n-octacosane.

for a small light molecule than for a large heavy molecule. For example, the diffusion coefficients for the gaseous solutes are much larger in magnitude than the corresponding alkane diffusion coefficients at the same conditions. Of the gaseous solutes, hydrogen, the smallest and lightest molecule, always diffuses the fastest. Similar behavior is seen with the alkane solutes. The smallest and lightest alkane solute studied was n-octane, and in every solvent it diffused faster than any other alkane, while n-hexadecane, the heaviest alkane studied, always diffused the slowest.

The effect of the solvent can be seen by comparing Figure 5.1 to Figure 5.3 and Figure 5.2 to Figure 5.4. Octacosane is a much larger and heavier molecule than either heptane or hexadecane. For this reason, at the same experimental conditions, diffusion coefficients for each solute are significantly smaller in the larger solvent n-octacosane than in any of the lower molecular weight solvents.

Diffusion coefficients for alkane and gaseous solvents in the Fischer-Tropsch wax are plotted versus temperature in Figure 5.5 and 5.6. Comparison of the Fischer-Tropsch plots to the corresponding n-octacosane plots, Figures 5.3 and 5.4, illustrates that the Fischer-Tropsch wax data not only follow the same general trends as the n-octacosane data but are close in magnitude as well. Later in this chapter, we will discuss this result in detail.

We were unable to measure the diffusion coefficient for hydrogen in the Fischer-Tropsch wax at 536 K because the hydrogen completely reacted in the diffusion tube. We had to inject up to 10 times the volume of a normal injection to even see peaks elute. When we did inject enough to see peaks, the peaks were greatly distorted, as if they may have contained a high molecular weight product. Surprisingly, we did not notice any unusual effects when measuring the diffusion coefficient for hydrogen at either 504 or 475 K. We can only surmise that either the wax contained

catalyst fines even though it was delivered pre-filtered, the diffusion tube (stainless steel) acted as a catalyst, or that certain high molecular weight compounds were unstable at the highest temperature. Unfortunately, we were unable to pursue this problem because we feared that we might foul our diffusion tube with the reaction products. Following the completion of the Fischer-Tropsch experiments, we repeated selected measurements in the solvent n-hexadecane. Both density and diffusivity measurements agreed within experimental error with measurements made prior to the Fischer-Tropsch experiments. These results confirmed that significant coking or fouling had not occurred.

Table 5.5 reports the viscosity and density of the solvents n-heptane, n-dodecane, and n-hexadecane at the same experimental conditions given in Tables 5.1 and 5.2. The dodecane and hexadecane viscosity and density were measured as a part of this work using the techniques described in Chapter IV. For heptane, viscosities (Stephan and Lucas, 1979) and densities (Orwell and Flory, 1967) were available in the literature at all experimental conditions, and were not measured. These values of density and viscosity for heptane are included in Table 5.5 to show explicitly which values were used in the analysis of diffusion data.

As with any experimental work, comparison with available data is desirable and in Tables 5.6 and 5.7 our measured densities and viscosities are compared with literature values. The agreement between the present data is excellent where comparisons are possible. Note that there are no density data available at temperatures above 443 K, and no viscosity data above 460 K. For hexadecane, the comparisons are with viscosities measured at atmospheric pressure. The effect of higher pressure is to increase the viscosity, which is the trend shown in Table 5.5. Because the measured and literature values are not at the same conditions for

ALKANES IN FISCHER-TROPSCH WAX
475 TO 537 K, 200 psia

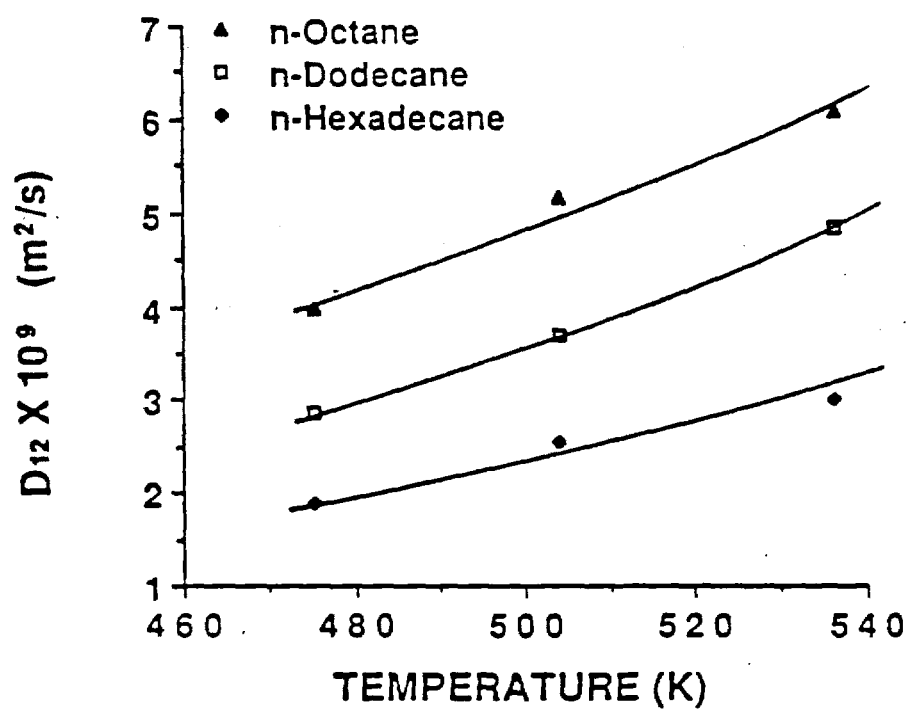


Figure 5.5. Diffusion coefficients for n-alkanes in Fischer-Tropsch wax.

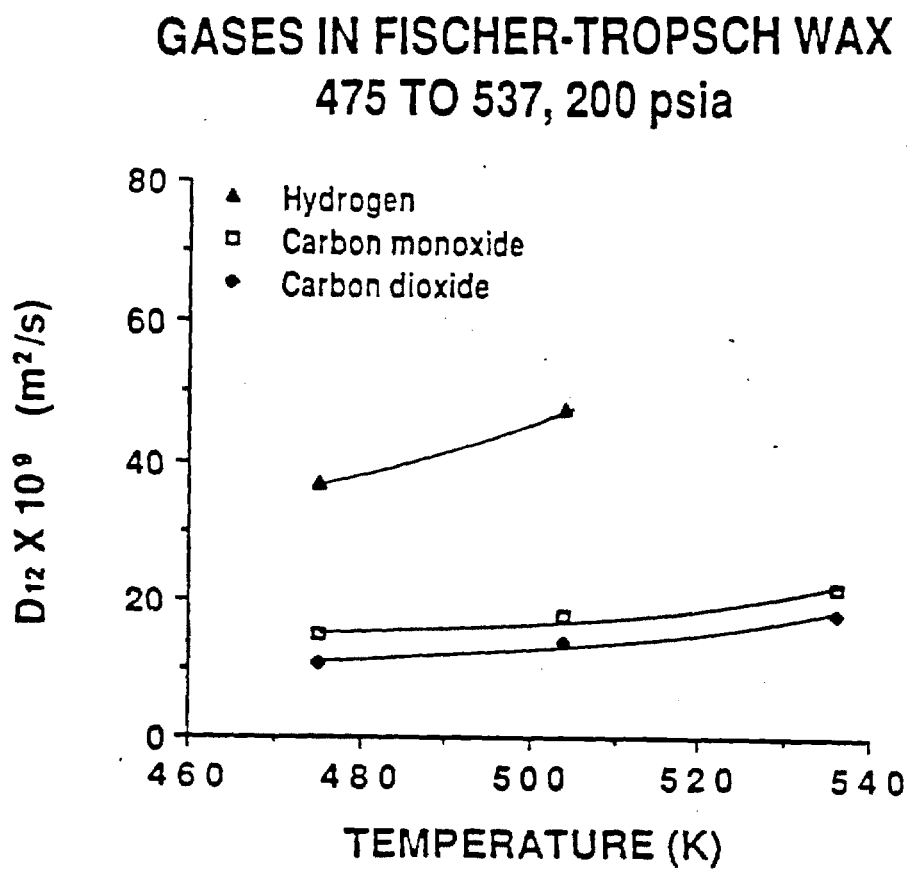


Figure 5.6. Diffusion coefficients for gases in Fischer-Tropsch wax.

Table 5.5. Viscosity and Density of n-Heptane, n-Dodecane, and n-Hexadecane

T (K)	P (kPa)	ρ (10^{-3} kg/m ³)	η (10^3 Pa·s)
Solvent: n-Heptane			
298	101	0.6794 ¹	0.390 ²
298	3550	0.6828	0.406
300	1894	0.6776	0.389
374	379	0.6127	0.196
374	3476	0.6181	0.205
427	710	0.5578	0.127
427	3461	0.5675	0.134
476	1410	0.5019	0.085
476	3482	0.5185	0.092
Solvent: n-Dodecane			
304	1413	0.7422 ³	1.259 ⁴
373	1413	0.6916	0.526
373	3443	0.6929	0.532
443	1446	0.6366	0.287
443	3454	0.6396	0.293
513	1448	0.5780	0.186
515	3434	0.5818	0.191
566	1462	0.5231	0.141
566	3440	0.5318	0.155
Solvent: n-Hexadecane			
323	1420	0.7528 ³	1.887 ⁴
323	3459	0.7536	1.921
371	1402	0.7203	0.949
371	3444	0.7216	0.953
443	1383	0.6693	0.459
443	3425	0.6725	0.478
514	1412	0.6162	0.275
514	3427	0.6171	0.278
564	1404	0.5748	0.195
564	3408	0.5811	0.214

1. Calculated from Orwoll and Flory (1967). Estimated uncertainty 0.0002×10^{-3} kg/m³.

2. Interpolated from Stephan and Lucas (1979). Estimated uncertainty 5% of the reported value.

3. Measured in this work. Estimated uncertainty 0.2% of the reported value.

4. Measured in this work. Estimated uncertainty 3% of the reported value.

Table 5.6. Comparison of Measured Densities with the Correlation of Orwoll and Flory (1967).

T (K)	P (kPa)	Measured ρ (10^{-3} kg/m ³)	Literature ρ (10^{-3} kg/m ³)	Error ¹ (%)
Solvent: n-Dodecane				
304	1413	0.7422	0.7422	0
373	1413	0.6916	0.6921	-0.07
373	3443	0.6929	0.6938	-0.13
443	1446	0.6366	0.6374	-0.13
443	3454	0.6396	0.6409	-0.20
Solvent: n-Hexadecane				
323	1420	0.7528	0.7539	-0.15
323	3459	0.7536	0.7554	-0.24
371	1402	0.7203	0.7207	-0.06
371	3444	0.7216	0.7227	-0.15
443	1383	0.6693	0.6693	0.0
443	3425	0.6725	0.6726	-0.01

1. Error = $100 \times (\text{Measured} - \text{Literature})/\text{Literature}$

Table 5.7. Comparison of Measured Viscosities with Literature Values

T (K)	P (kPa)	Measured η (10^3 Pa·s)	Literature η (10^3 Pa·s)	Error ¹ (%)
Solvent: n-Dodecane				
304	1413	1.259	1.259 ²	0
373	1413	0.526	0.524	+0.4
373	3443	0.532	0.538	-1.1
443	1446	0.287	0.284	+1.1
443	3454	0.293	0.291	+0.7
Solvent: n-Hexadecane				
323	1420	1.887	1.867 ³	-
371	1402	0.949	0.922	-
443	1383	0.459	0.4521	-

1. Error = $100 \times (\text{Measured} - \text{Literature})/\text{Literature}$

2. Stephan and Lucas (1979).

3. TRC Thermodynamic Tables (1986). All values at atmospheric pressure = 101.4 kPa.

Table 5.8. Density of n-Eicosane, and n-Octacosane, and Fischer-Tropsch Wax

T (K)	P (kPa)	ρ (10^{-3} kg/m ³)
Solvent: n-Eicosane		
375	1380	0.735
413	1410	0.712
454	1400	0.684
495	1380	0.654
534	1320	0.626
Solvent: n-Octacosane		
373	1430	0.756
413	1380	0.734
454	1380	0.705
495	1390	0.675
534	1370	0.651
Solvent: Fischer-Tropsch Wax		
454	1400	0.700 ¹
475	1400	0.687
495	1400	0.675 ²
504	1400	0.669
534	1400	0.645 ²
536	1400	0.643

1. Obtained from linear extrapolation of actual data. 2. Obtained from linear interpolation of actual data.

hexadecane, the error is not calculated.

After we completed our data collection in the solvents n-heptane, n-dodecane, and n-hexadecane, we examined several forms of correlations for the diffusion coefficient and decided not to pursue a correlation which required viscosity data. For this reason, we decided not to collect viscosity data in the solvents which are solid at room temperature. However, we did collect density data at all experimental conditions for the solvents n-eicosane, n-octacosane, and Fischer-Tropsch wax. This data is presented in Table 5.8. This is the first reported density data for n-eicosane and n-octacosane at these conditions, and is likely the only density data for an actual sample of Fischer-Tropsch wax at reactor conditions. Values of density which

correspond to the experimental conditions for n-eicosane, and n-octacosane were interpolated from the actual Fischer-Tropsch wax data and are included in Table 5.8. As was the case with the diffusion coefficients, the densities of the Fischer-Tropsch wax are in close agreement with the densities of the pure n-octacosane. This result further confirms that the average molecular weight of the wax is indeed near that of n-C₂₈.

The results of this section represent the first use of an apparatus for simultaneous measurement of mutual diffusion coefficients, solvent density, and solvent viscosity. It is evident that a large quantity of accurate data can be generated from such an apparatus. This has significant implications for future development of theories for comprehensive treatment of thermophysical properties, because data for several properties are required to verify such theories.

5.2 Evaluation of Existing Predictive Equations

Several available predictive equations were discussed in Chapter 2. Most of these equations were developed from low temperature experimental data. In this section, several of these equations are evaluated using the new high temperature data provided by this study.

Figure 5.7 shows the measured diffusivities of n-octane, and the values calculated from several different equations. The values shown are for the solvent n-hexadecane at a pressure of approximately 1400 kPa (205 psia). The octane/hexadecane system is typical of all alkane/alkane systems, and the errors for other solutes are of the same order of magnitude and show the same trends. It is seen that the three hydrodynamic equations (Wilke-Chang, Lysis-Ratcliff, and Chen-Chen) systematically underpredict at low temperatures and overpredict at

high temperatures. These fail because they are based on the principle that $D_{12}\eta/T$ is constant, when in reality it is a decreasing function of temperature. This well known discrepancy is illustrated for octane/hexadecane in Figure 5.8. The Shieh and Lyons correlation, which gives diffusivity as a function of density, fails miserably except at room temperatures. The equation suggested by Lo relates mutual diffusion to the self-diffusion coefficient of the solvent. This equation also underpredicts the observed diffusivity. In addition, data for self-diffusion of alkanes is available only to about 443 K (Ertl and Dullien, 1973), so this relation is not extended beyond that temperature in Figure 5.7. We conclude from Figure 5.7 that the hydrodynamic approaches are the only ones which reasonably follow the observed temperature dependence, and these require viscosity data which may not be available. However, the theoretical premise for these is not valid over extended temperature ranges, as shown by Figure 5.8.

The measured diffusivities of hydrogen and carbon monoxide are compared to the predictions from the Wilke-Chang, Sovova, and Akgerman-Gainer equations in Figure 5.9 and 5.10. The behavior of these equations for carbon dioxide was found to be qualitatively the same as for carbon monoxide. It is seen that predictions of gas diffusivities from the Wilke-Chang and Sovova correlations are too low. The Akgerman-Gainer equation is better for carbon monoxide; however for hydrogen it underpredicts at low temperatures and overpredicts at high temperatures. Examination of these equations reveals that the adjustable physical parameter in each of these is the volume of the solute, and there is no single value of volume which could bring the calculated values in line with the measured values. It is again evident that the diffusion of gases in liquids at high temperatures is not handled well by existing theories.

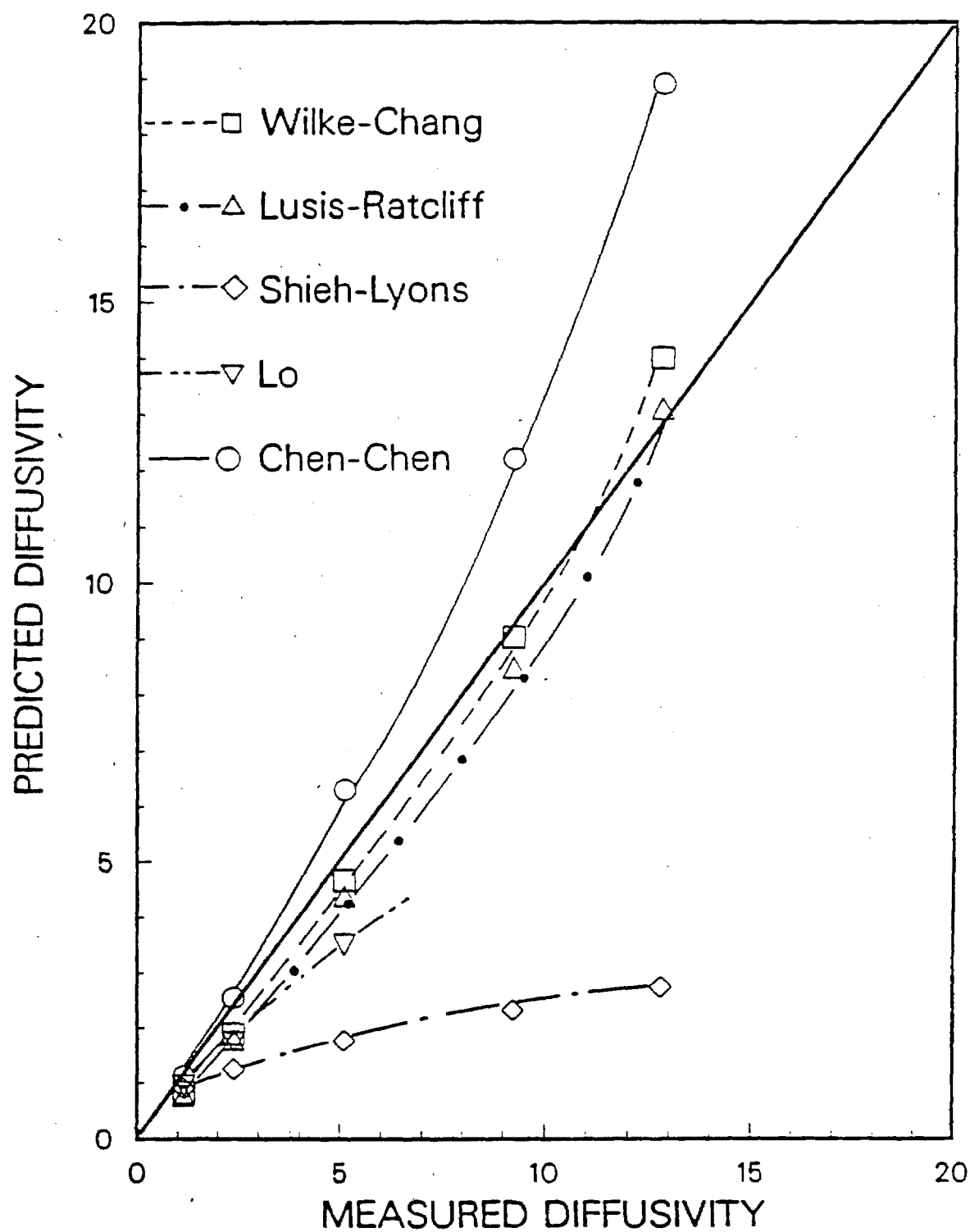


Figure 5.7. Comparison of measured diffusivities to calculated diffusivities of octane in hexadecane. Diffusivities in $10^9 \text{ m}^2/\text{s}$.

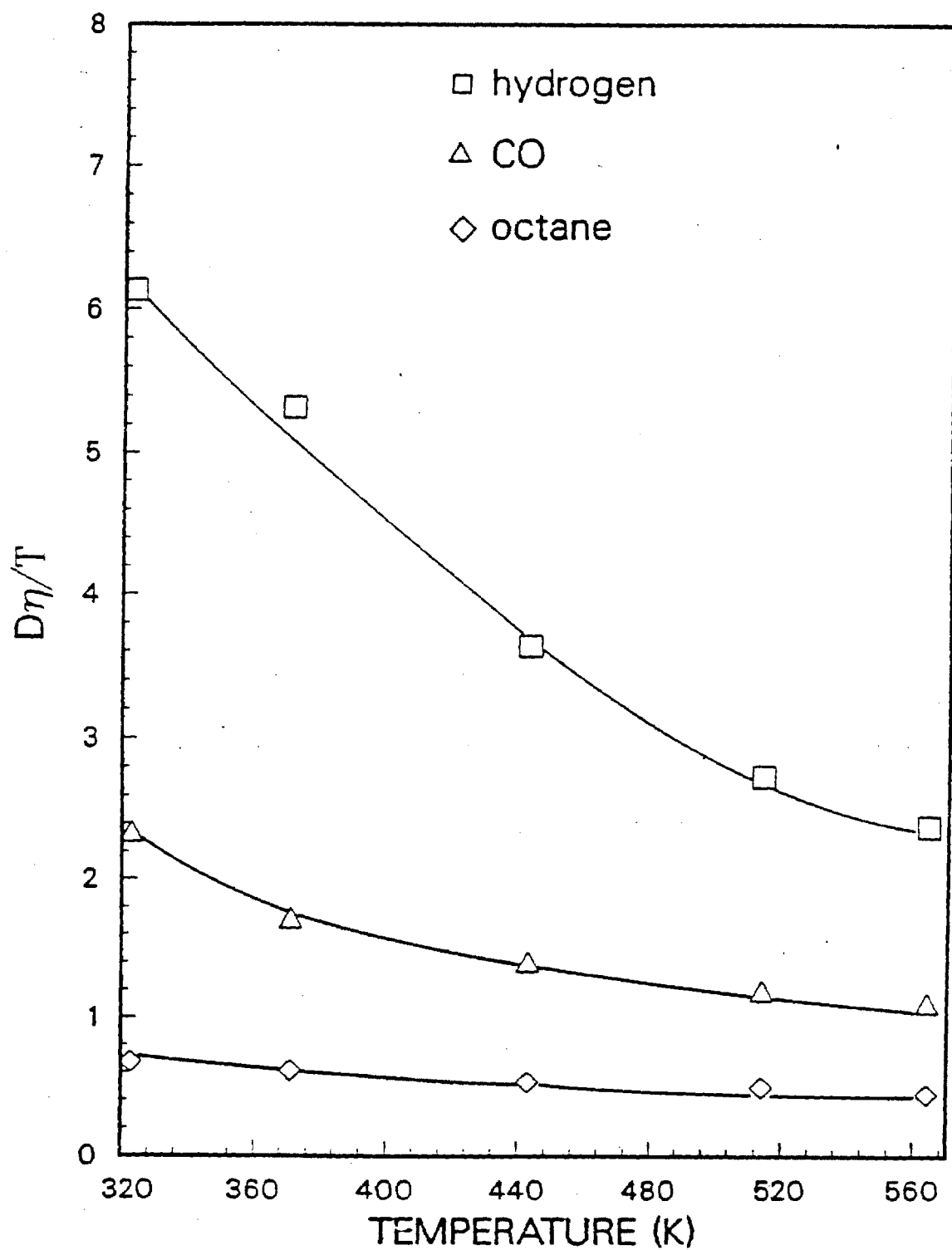


Figure 5.8. Behavior of the hydrodynamic group $D_{12}\eta/T$ with increasing temperature. D_{12} in $10^9 \text{ m}^2/\text{s}$, η in $10^3 \text{ Pa}\cdot\text{s}$, T in Kelvins.

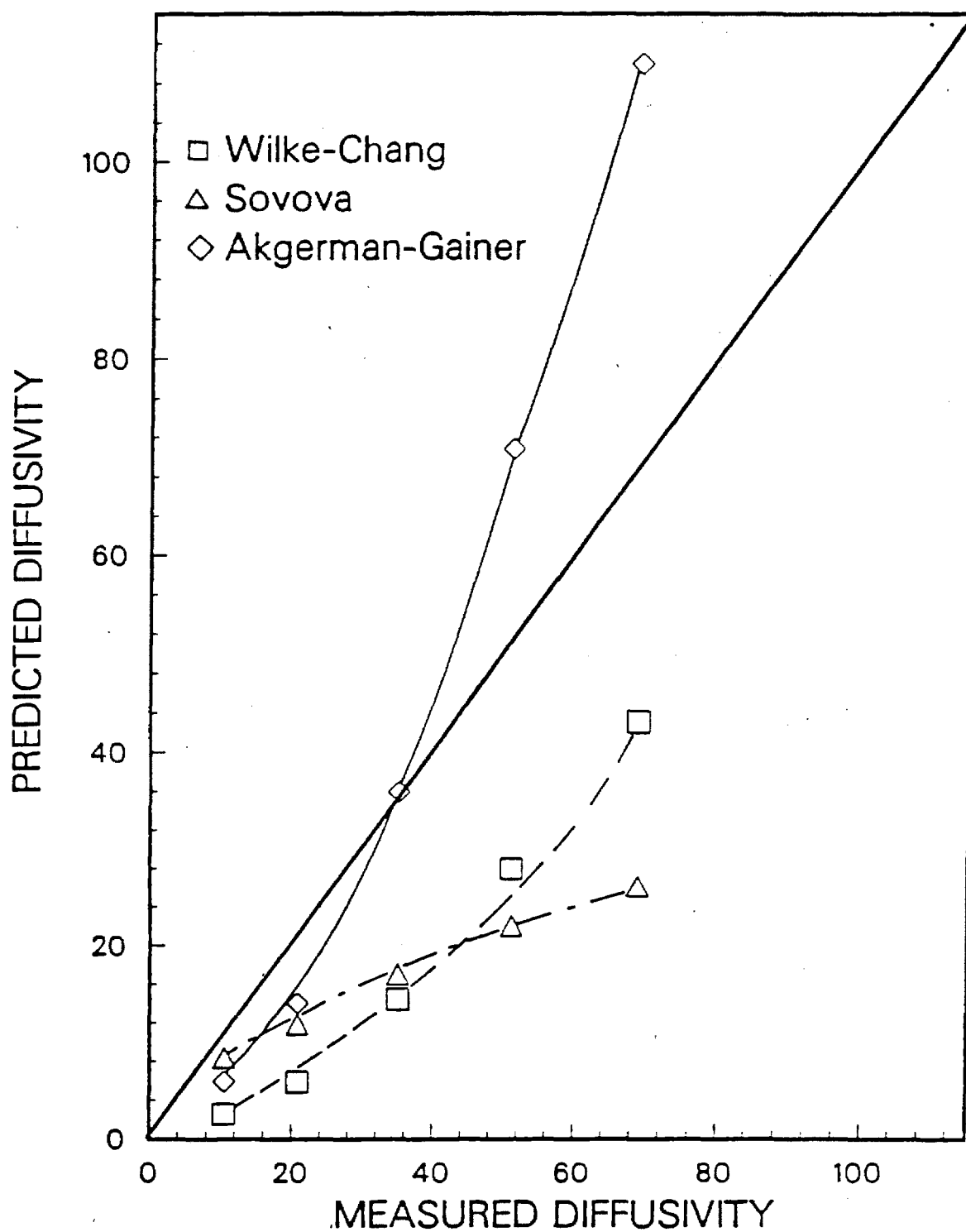


Figure 5.9. Comparison of measured hydrogen diffusivities to predictions from several equations. Diffusivities in $10^9 \text{ m}^2/\text{s}$.

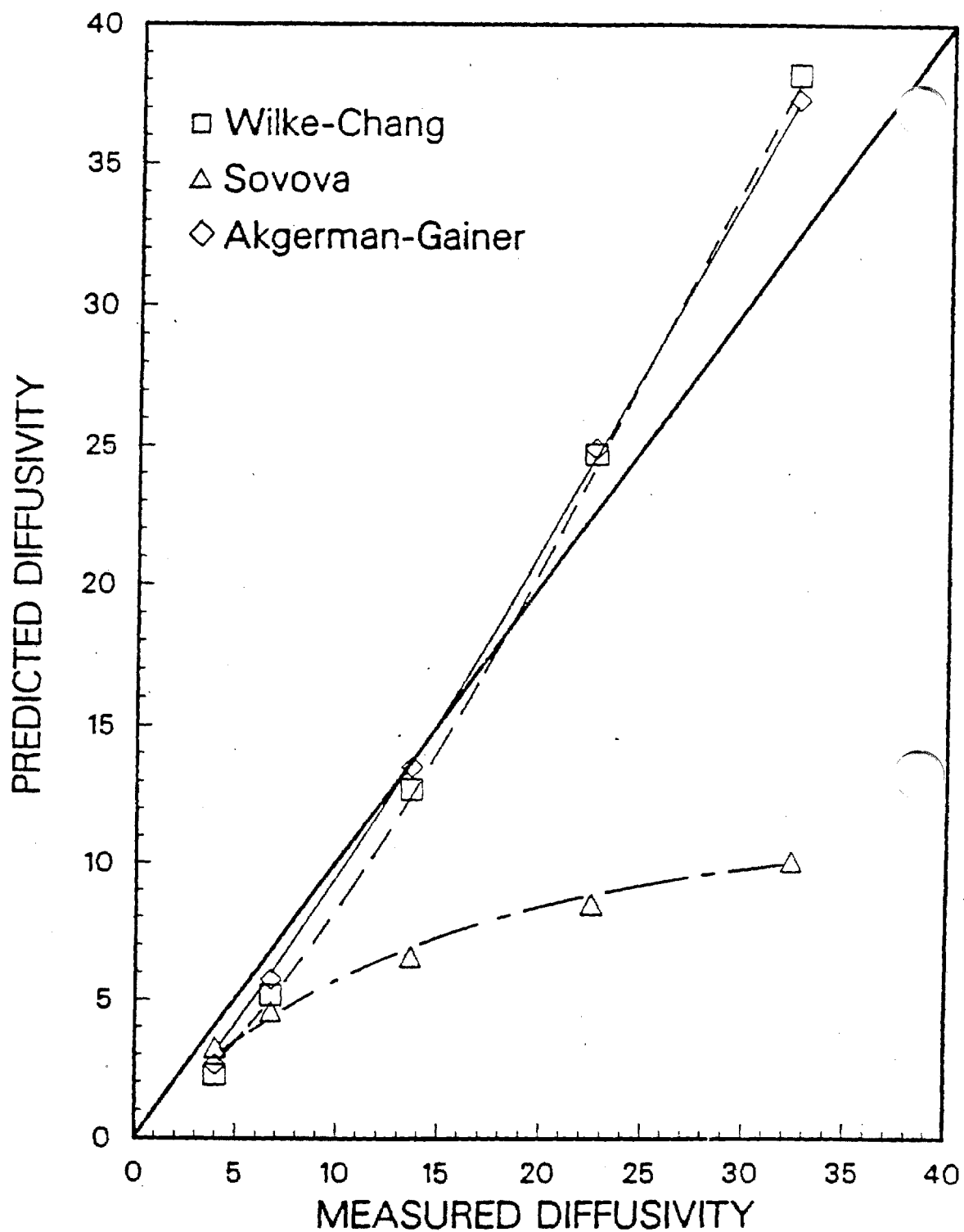


Figure 5.10. Comparison of measured carbon monoxide diffusivities to predictions from several equations. Diffusivities in $10^9 \text{ m}^2/\text{s}$.

5.3. Rough Hard Sphere Treatment of Diffusivity

According to the rough hard sphere (RHS) theory outlined in Chapter III, the temperature dependence of the diffusion coefficient should follow the form of Equation 3.15:

$$\frac{D_{12}}{\sqrt{T}} = \beta(V - V_D) \quad (3.15)$$

Should this relationship hold, then it would be possible to predict D_{12} for a given solute/solvent pair by using one temperature dependent physical property (the solvent molar volume V) and two constants, β and V_D . From the standpoint of practicality, the resulting equation would be easier to use than any previous equation, and as discussed in Chapter III, the RHS theory has a more solid fundamental basis than hydrodynamic or activated state theory. For these reasons, we decided to investigate the RHS approach in detail.

In Figures 5.11 through 5.14, D_{12}/\sqrt{T} is plotted against the solvent molar volume V for the same solute-solvent systems which were plotted in Figures 5.1 through 5.4. There is indeed a linear relationship which confirms the predictions of the RHS theory. Equation 3.15 has a sound theoretical basis which is confirmed by the experimental data, and is simple enough to use for predictive purposes. Therefore we continue examination of the intercept volume V_D and the slope β to determine how these parameters might be predicted a priori.

The constants β and V_D for each solvent pair are given in Tables 5.9 and 5.10. The intercepts V_D , as determined from regression analysis, are a strong function of the solvent, as expected. However, V_D also depends weakly on the solute. The gaseous solutes, which are much smaller and lighter than the alkanes, always yield intercepts which are consistently lower than the alkane intercepts. Hydrogen, the smallest solute, has the lowest intercept for nearly every solvent. The same trend

DIFFUSIVITY OF ALKANES IN N-HEPTANE
298 TO 476 K, 500 psia

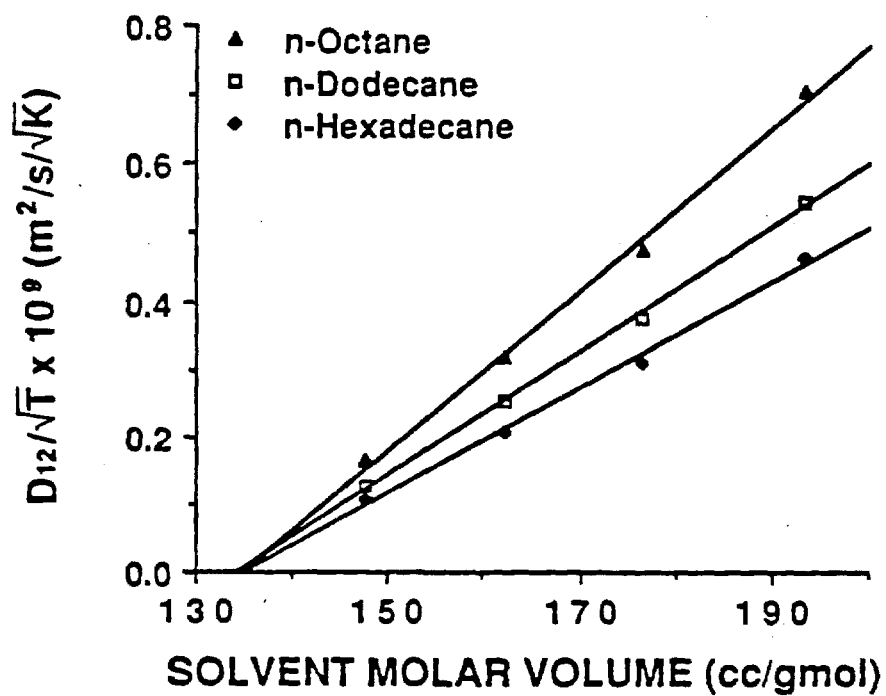


Figure 5.11. Demonstration of Equation 3.15 for alkane diffusion in heptane.

DIFFUSIVITY OF GASES IN N-HEXADECANE
323 TO 564 K, 200 psia

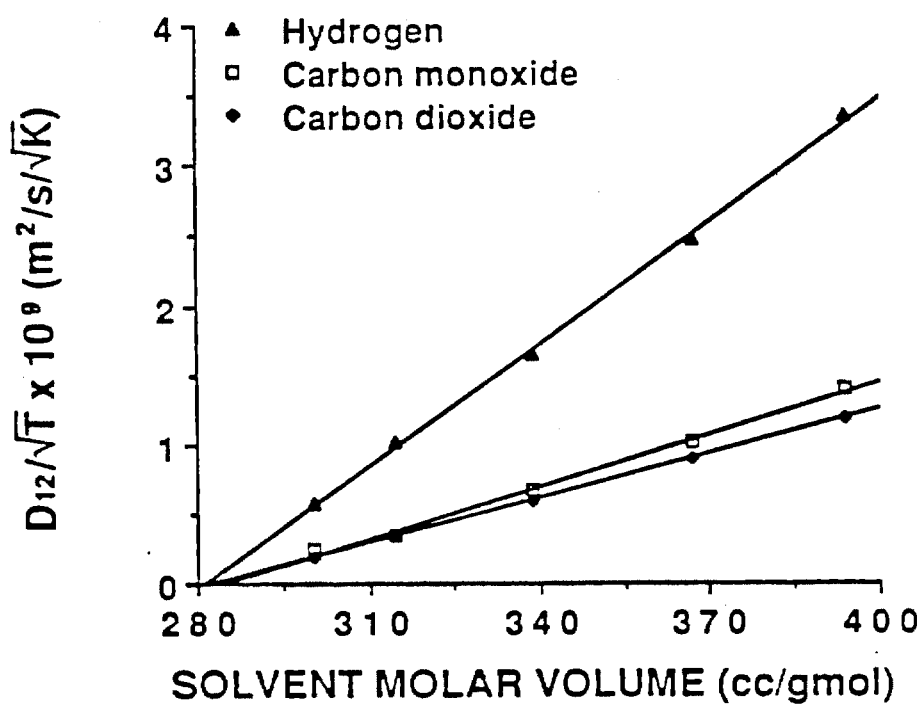


Figure 5.12. Demonstration of Equation 3.15 for gas diffusion in hexadecane.

DIFFUSIVITY OF ALKANES IN N-OCTACOSANE
372 TO 535 K, 200 psia

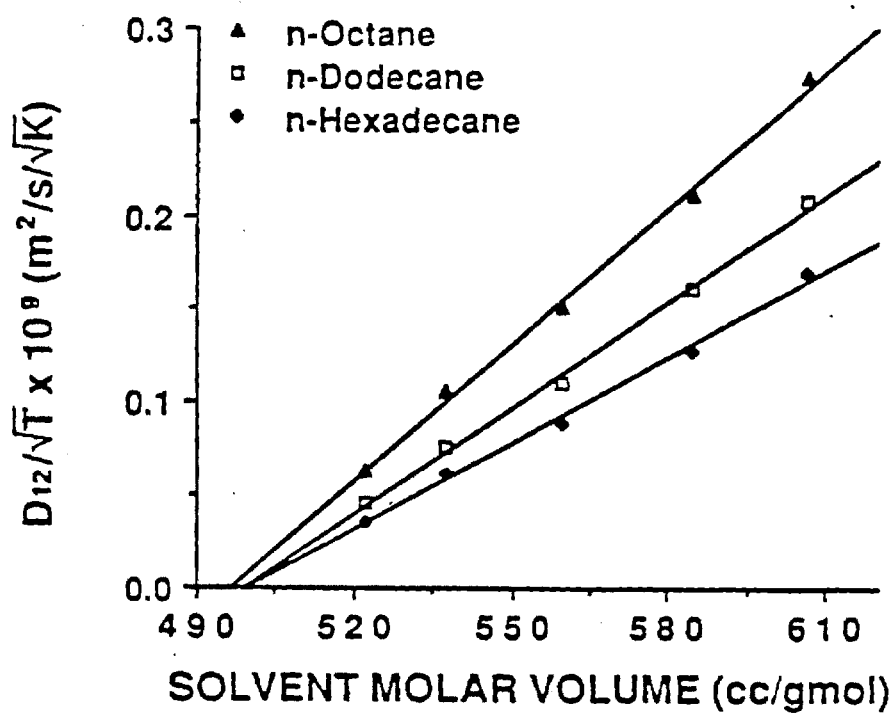


Figure 5.13. Demonstration of Equation 3.15 for alkane diffusion in octacosane.

DIFFUSIVITY OF GASES IN N-OCTACOSANE 371 TO 534 K, 200 psia

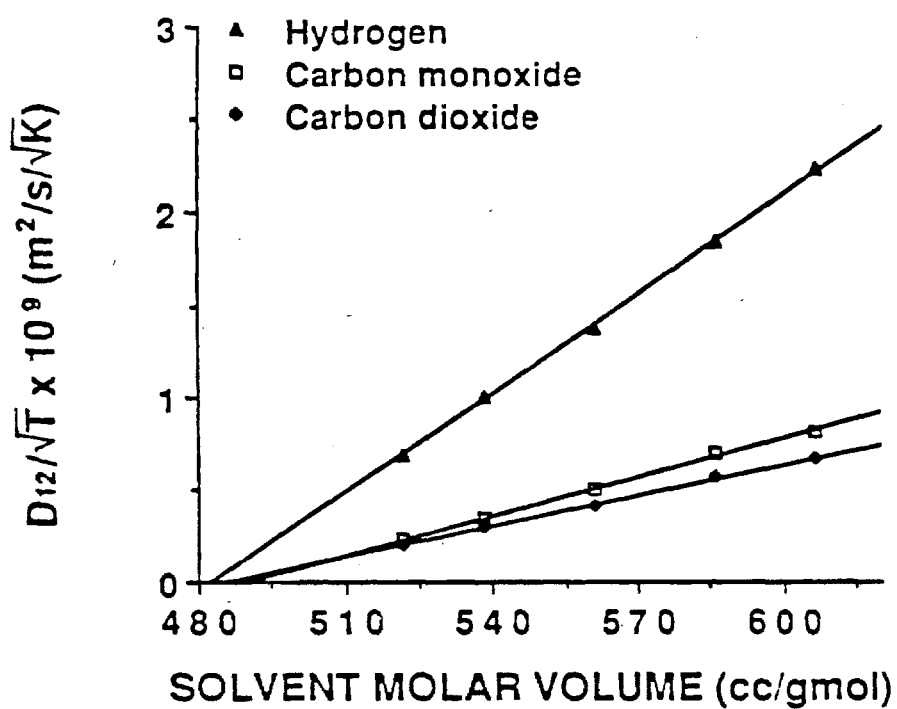


Figure 5.14. Demonstration of Equation 3.15 for gas diffusion in octacosane.

appears to be present for the alkane solutes. For most solvents, the intercepts increase with solute size and weight, although the trend is difficult to describe quantitatively because the intercepts are often within experimental error of each other. The general trend observed for the intercepts can be explained by the fact that smaller solutes are more mobile than larger solutes, even in the limited free volume available for diffusion near the freezing point.

The values of the solvent liquid volumes at their respective triple points are also given in Tables 5.9 and 5.10. It is seen that V_D is very close to V_{tp} . Physically this implies that the diffusion coefficient goes to zero at the point where the solvent is making the phase change from liquid to solid. This is exactly what one would expect, since diffusion coefficients in solids are orders of magnitude lower than those in liquids. It is noted that some of the intercept volumes are actually lower than the liquid triple point volume. This may be due to experimental uncertainty, but is more likely due to our lack of knowledge concerning diffusion near the freezing temperature of liquids. We do not imply that diffusion at rates typical of liquids will continue below the temperature at which the solvent freezes. The behavior of the diffusion coefficient near the freezing point is known to be complex, and is not the topic of this work. The experimental data for this study was collected at temperatures well above the triple points of the solvents. In order to fully understand diffusion near the freezing point, data at lower temperatures are required.

Equation 3.14 for self-diffusion predicts that V_D is given by the following simple relationship, where b is a constant, N is Avogadro's number, and V_0 is the theoretical close-packed volume for solvent spheres of diameter σ_2 ;

$$V_D = bV_0 = bN\sigma_2^3/\sqrt{2} \quad (5.1)$$

Table 5.9. Coefficients for Linear Regression of Diffusivity Data
for n-Heptane, n-Dodecane, and n-Hexadecane
Using Equation 3.15

$$10^9 D_{12} / \sqrt{T} = \beta(V - V_D)$$

(D_{12} in m^2/s , T in K, V in $10^{-6} \text{ m}^3/\text{mol}$)

Solute	β	V_D ($10^{-6} \text{ m}^3/\text{mol}$)
--------	---------	---

Solvent: n-Heptane, $V_{tp}=129^1$.

n-octane	0.01181	134.8
n-decane	0.01017	134.7
n-dodecane	0.009126	134.2
n-tetradecane	0.008623	136.3
n-hexadecane	0.007844	135.1
H ₂	0.06473	128.9
CO	0.02757	134.1

Solvent: n-Dodecane, $V_{tp}=221.2$

n-octane	0.006830	220.0
n-decane	0.005908	220.1
n-tetradecane	0.004828	223.1
n-hexadecane	0.004611	225.4
H ₂	0.04301	215.8
CO	0.01637	215.4
CO ₂	0.01412	214.4

Solvent: n-Hexadecane, $V_{tp}=292.0$

n-octane	0.005351	290.4
n-decane	0.005139	293.3
n-dodecane	0.004120	289.5
H ₂	0.02928	281.2
CO	0.01259	284.7
CO ₂	0.01072	282.6

V_{tp} = liquid triple point volume; in $10^{-6} \text{ m}^3/\text{mol}$.

Table 5.10. Coefficients for Linear Regression of Diffusivity Data
for n-Eicosane and n-Octacosane
Using Equation 3.15

$$10^9 D_{12}/\sqrt{T} = \beta(V - V_D)$$

(D_{12} in m^2/s , T in K, V in $10^{-6} \text{ m}^3/\text{mol}$)

Solute	β	V_D ($10^{-6} \text{ m}^3/\text{mol}$)
--------	---------	---

Solvent: n-Eicosane, $V_{tp}=363.7^1$.

n-octane	0.03945	361.3
n-decane	0.03409	361.8
n-dodecane	0.003067	362.9
n-tetradecane	0.002693	362.7
n-hexadecane	0.002470	363.2
H ₂	0.02604	351.6
CO	0.01012	356.1
CO ₂	0.008629	353.2

Solvent: n-Octacosane, $V_{tp}=503$.

n-octane	0.02445	496.5
n-dodecane	0.001901	498.7
n-hexadecane	0.001541	499.5
H ₂	0.01788	482.5
CO	0.007073	489.2
CO ₂	0.005572	484.9

V_{tp} = liquid triple point volume; in $10^{-6} \text{ m}^3/\text{mol}$.

We calculated values for σ using the method of Bondi (1964) which is based on experimental x-ray diffraction data. All values for σ used in this study are given in Table 5.11. We observed that the constant in Equation 5.1, b , was actually a weak function of the solute size. Using simple least squares analysis, we developed the following formula for b which fits our intercepts in Tables 5.9 and 5.10 quite well;

$$b = 1.206 + 0.0632(\sigma_1/\sigma_2) \quad (5.2)$$

This formula reduces to the constant 1.269 for the case of self diffusion, where σ_1 equals σ_2 . We found that with b equal to 1.269, Equation 5.1 agrees closely with the triple point volume for each solvent, as shown in Table 5.12. This agreement

confirmed that the constant has a strong theoretical basis, since the intercepts for self diffusion are expected to be near the melting points of the solvents.

We have shown a simple method for calculating the intercept volume V_D a priori. The more difficult task is to explain and predict the multiplier β . The linear relationship given by Equation 3.15 has been observed by Chen and Chen (1985b), but a systematic investigation of β has never been attempted. This study provided enough information to allow for such an investigation.

We now recall some of the physical bases for the RHS theory as given in Chapter III. Equation 3.15 is based on a treatment of the computer-generated values of the terms given in Equation 3.13. Chen (1981) compiled all available computer calculations for mutual diffusion, which comprised only 41 calculations over an incomplete grid bounded by $0.01 \leq m_1/m_2 \leq 4$, $0.5 \leq \sigma_1/\sigma_2 \leq 1.6$, and $1.5 \leq V/V_o \leq 3.0$. These values were chosen because they were a reasonable bound for the sizes and shapes of most simple molecules. At molar volumes below $1.5 V_o$, these computer simulations have indicated that RHS theory breaks down, while above $3V_o$ the simpler Enskog theory is adequate.

In this work, m_1/m_2 ranges from a high of 2.26 for the C_{16}/C_7 system to a low of 0.0051 for the H_2/C_{28} system. The diameter ratio ranges from about 1.3 to 0.30 for the same two systems. Using the measured values of V , which is simply the molecular weight divided by the density, we calculate an experimental range for V/V_o of 1.4 to 2.0. It is clear that much of the experimental data in this work is outside the range where computer simulations have been performed. Also, for the gases (particularly H_2), the mass and size ratios are in the range where few simulated data are available. Therefore, this work establishes experimentally that the RHS treatment is valid for regions outside of those studied by computer simulations.

Table 5.11 Molecular Diameters and Weights for All Solutes and Solvents

Compound	σ (Angstroms)	M (gm/mol)
H ₂	2.92	2.016
CO	3.72	28.01
CO ₂	3.97	44.01
n-C ₇ H ₁₆	6.29	100.2
n-C ₈ H ₁₈	6.55	114.2
n-C ₁₀ H ₂₂	7.00	142.3
n-C ₁₂ H ₂₆	7.44	170.3
n-C ₁₄ H ₃₀	7.81	198.4
n-C ₁₆ H ₃₄	8.15	226.5
n-C ₂₀ H ₄₂	8.75	282.5
n-C ₂₈ H ₅₈	9.76	394.8
n-C _j H _{2j+2}	$(21.82 + 32.44j)^{1/3}$	$14.027j + 2.016$

NOTE: Molecular diameters were calculated using Bondi's (1964) method.

Table 5.12 Comparison of Solvent Limiting Molar Volumes (cm^3/gmol)

Solvent	V_D	$1.27 V_0$	V_{tp}
n-C ₇ H ₁₆	129 - 136	135	129.3
n-C ₁₂ H ₂₆	214 - 225	222	221.2
n-C ₁₆ H ₃₄	281 - 290	293	292.2
n-C ₂₀ H ₄₂	352 - 363	363	363.7
n-C ₂₈ H ₅₈	483 - 500	503	503.0

Since there is no explicit representation of the slope in Equation 3.15, we used the experimental data to establish a method of predicting the slope β . This constant contains all the information on the interactions between unlike particles 1 and 2. RHS theory suggests β is some function of the following variables: solute and solvent molecular masses, or possibly the reduced mass $(m_1 + m_2)/m_1 m_2$; the volume V_D , and the molecular diameters. In seeking a representation for the slope β , several requirements were enforced. First, we required an equation with as few parameters as possible, with each parameter indicating a high level of statistical significance. We also required that only the variables suggested by RHS theory be employed in the correlation; thus arbitrary use of viscosity or activation energy was not allowed. Our goal was to correlate gas and alkane diffusion coefficients in a single correlation, although at the onset of our work we were not sure if this goal could be achieved.

We examined more than thirty ways of representing the multiplier β , using multiple linear regression. Several representations were found which adequately correlated β for either the gas or liquid solutes. However, only one representation satisfied all the criteria given in the paragraph above. We found that β for a given solute/solvent pair could be adequately represented by using only the following four

variables: the solute molecular weight, M_1 , the solvent molecular weight, M_2 , the solute diameter, σ_1 , and the solvent diameter, σ_2 . We found that the functional form of the slope β is predicted by the following equation;

$$\beta = \frac{a}{M_1^b M_2^c (\sigma_1 \sigma_2)^d} \quad (5.3)$$

Using the form of the slope given in Equation 5.3, we developed the following equation which summarizes the entire body of diffusion coefficient data which was collected during this study;

$$\frac{10^9 D_{12}}{\sqrt{T}} = \frac{94.5}{M_1^{0.239} M_2^{0.781} (\sigma_1 \sigma_2)^{1.134}} (V - bV_0) \quad (5.4)$$

In this equation, D_{12} is in m^2/s , T is in Kelvins, molecular weights are in gm/mol , and the molar volumes are in $10^{-6} \text{ m}^3/\text{mol}$. V_0 and b are given by Equations 5.1 and 5.2. The diameters σ_1 and σ_2 are in Angstroms and were given previously in Table 5.11 as calculated by the method of Bondi (1964). Bondi's method involves calculating the hard core volume of the molecule. From these volumes, the diameter of an equivalent volume sphere is easily calculated. We chose Bondi's method because it is the only consistent method available which allows the calculation of molecular diameters for several different groups of compounds.

Equation 5.4 predicts the data very well as shown by Figure 5.15. The average absolute percent deviation from the experimental data is 6.3%. The largest percentage errors occurred at low temperatures where the absolute value of the diffusion coefficients were quite low. In such cases, the magnitudes of the errors were often small, even though the percentage errors were relatively large. The general trends which were observed in the data are also predicted by Equation 5.4. In any given solvent, the equation predicts larger diffusion coefficients for

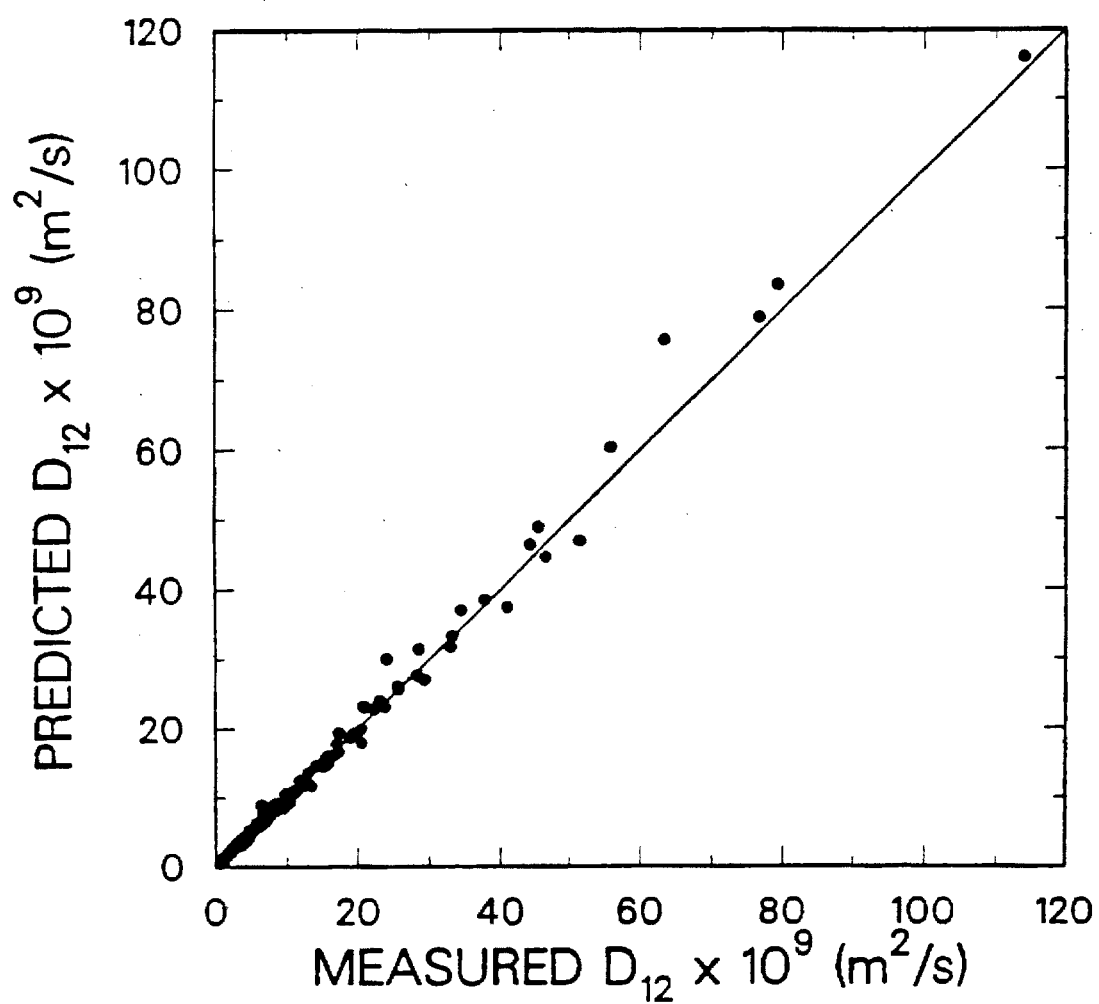


Figure 5.15. Comparison of measured diffusion coefficients to calculated values for all data in alkane solvents as predicted by Equation 5.4.

small, low-molecular weight solute molecules than for large heavy solute molecules. The equation also predicts that any given solute will diffuse faster through small low-molecular weight solvent molecules than through large, high-molecular weight molecules. Interestingly, Equation 5.4 quantitatively predicts the effects of solute and solvent molecular size to be identical.

In order to test the agreement of Equation 5.4 with the RHS theory, the equation can be written in the following form for self diffusion;

$$\frac{10^9 D_{22}}{\sqrt{T}} = \frac{49.6}{M_2^{1.020} V_0^{0.756}} (V - 1.269 V_0) \quad (5.5)$$

The general form of Equation 5.5 is identical to the form of Equation 3.14 which was developed by Dymond (1974) using computer calculations for self diffusion. The fact that these equations are similar is a further indication that our correlation has a strong fundamental basis. We will now discuss how the correlation may be used to estimate diffusion coefficients in Fischer-Tropsch reactor wax.

We have already noted that the average carbon number of the Fischer-Tropsch sample used for this study was near 28, and that the mixture was primarily normal alkanes, although some olefins and branched paraffins were also present in the sample. We have also shown that the diffusion coefficients and densities measured in the Fischer-Tropsch wax were similar in magnitude to the corresponding measurements in n-octacosane, which also has a carbon number of 28. For estimation purposes, we recommend using Equations 5.4 by treating the wax as a pure alkane with carbon number equal to the approximate average carbon number of the mixture. This treatment is not based purely on our data. Van Geet and Adamson (1964) have demonstrated that diffusion in alkane mixtures is a function of the average chain length of the mixture. There is also theoretical

justification for modelling chain molecules using average chain length (Prigogine et al., 1953).

The errors associated with using our suggested method decrease as the average carbon number increases. This point is illustrated by Figure 5.16 which shows the diffusion coefficients for the gaseous solutes as a function of pure alkane carbon number at the constant temperature of 475 K, as predicted by Equation 5.4. As carbon number increases, the model becomes less sensitive to carbon number. This result indicates that for high molecular weight solvents such as Fischer-Tropsch wax it is not crucial to know the average carbon number exactly. Figure 5.16 also illustrates the accuracy to which the model predicts diffusion in the Fischer-Tropsch wax when it is modelled as pure n-C₂₈.

Our suggested method is bound to raise some concern regarding the effect of olefins on the diffusion coefficients in Fischer-Tropsch wax. Olefins are smaller and lighter than the corresponding alkanes with the same carbon number. For this reason, the presence of olefins tends to increase the diffusion coefficient for all solutes. This explains why several of our measurements in the Fischer-Tropsch wax are slightly larger than the corresponding interpolated measurements in n-octacosane at the same conditions. The reason that the olefins in the sample did not affect the measured diffusion coefficients to a greater degree is that most of the olefins were mono-olefins, with similar properties to the corresponding n-alkanes. For design purposes, it is prudent to assume that the Fischer-Tropsch wax is a pure alkane, since this assumption will result in a conservative (low) estimate of the predicted diffusion coefficients.

Many Fischer-Tropsch waxes contain a much higher percentage of oxygenates than the Union Carbide wax. Oxygenates are heavier and larger molecules

DIFFUSIVITY OF GASES IN N-ALKANES AND
IN FISCHER-TROPSCH WAX AT 475 K

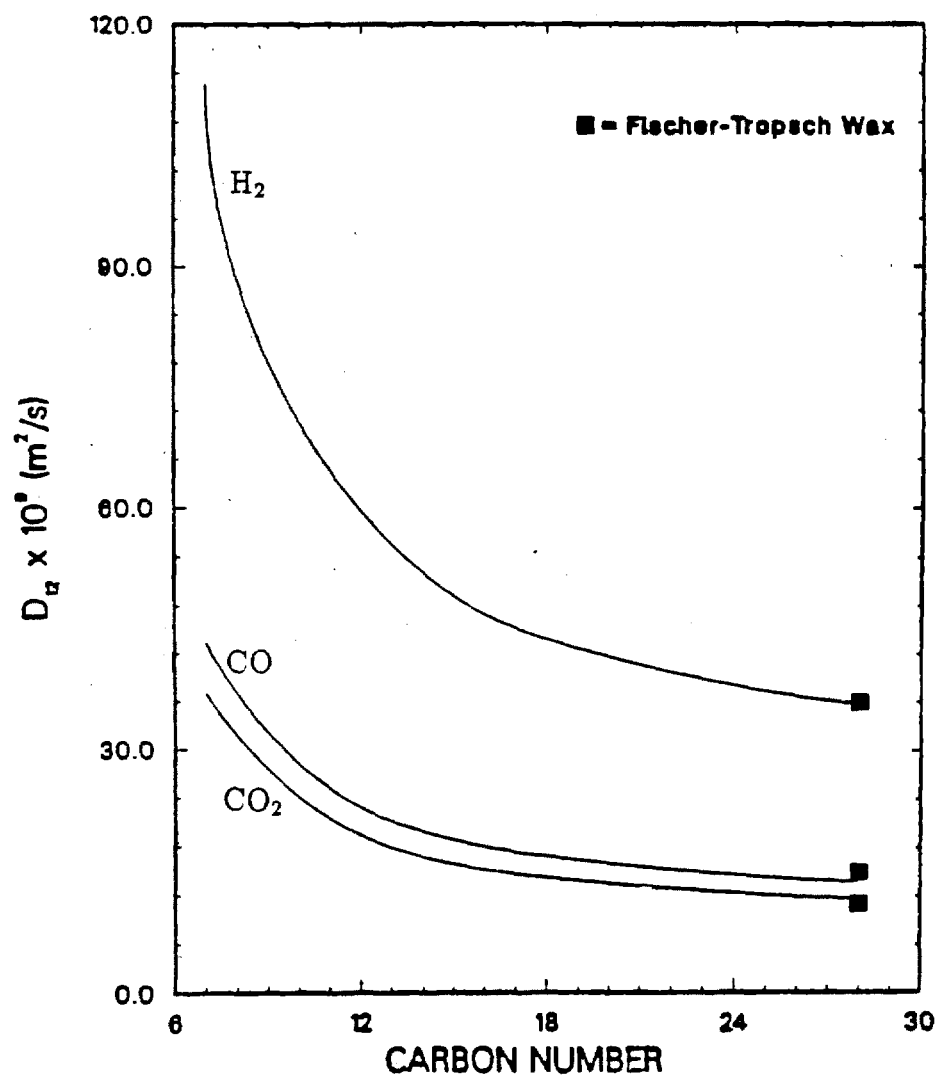


Figure 5.16. Diffusivity of gases as a function of carbon number at 475 K, predicted by Equation 5.4.

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than corresponding alkanes with the same carbon number. For this reason, the presence of oxygenates would likely decrease diffusion coefficients as compared to measurements in a pure alkane. In Chapter VII we discuss recommendations for future work to develop a method of quantitatively predicting diffusion coefficients as a function of mixture composition.