

## CHAPTER VII

## RESULTS AND DISCUSSION

This chapter presents all of the diffusion coefficients and densities measured during the course of this work. Diffusion coefficients from the previous work at Texas A&M in the solvents *n*-heptane, *n*-dodecane, and *n*-hexadecane have also been recalculated using the improved analysis method, and results are presented herein. Finally, a correlation for diffusion in *n*-alkanes is presented which was developed using the data from both this work and the previous work. Recommendations are given for using this correlation to predict diffusion coefficients in Fischer-Tropsch reactor wax. Currently used estimates of diffusion in Fischer-Tropsch wax were found to be grossly in error.

## A. DIFFUSION COEFFICIENTS MEASURED DURING THIS WORK

Since previous measurements have indicated that diffusion in alkane solvents is a very weak function of pressure over the range 0-500 psi, (Matthews and Akgerman, 1987a), all measurements for this study were made at 200 psia (1400 kPa), which is a typical operating pressure of a Fisher-Tropsch reactor. For the solvents *n*-eicosane and *n*-octacosane, solvent density and diffusion coefficients for all solutes were measured at approximately 100, 140, 180, 220, and 260°C. For the Fischer-Tropsch wax, data were collected at approximately 200, 220, 240, 260°C, in order to cover the normal range of Fischer-Tropsch reaction temperatures.

Table 7.1 includes the diffusion coefficients for the alkane solutes *n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane, in the solvents *n*-eicosane, *n*-octacosane, and Fischer-Tropsch reactor wax. at approximately 1400 kPa (200 psi). Diffusion coefficients for the gaseous solutes hydrogen, carbon monoxide,

and carbon dioxide were measured at approximately the same conditions and are reported in Table 7.2. Most entries in these tables represent the average of at least three repetitive measurements. Each reported uncertainty represents one standard deviation corrected for the total number (usually 3) of repetitive measurements.

Figures 7.1 through 7.4 illustrate the effects of temperature, and solute and solvent characteristics on the infinite dilution diffusion coefficient. The data from Tables 7.1 and 7.2 were plotted as a function of temperature for the solvents n-eicosane, ( $C_{20}$ ) and n-octacosane ( $C_{28}$ ) to illustrate several trends which are indicative of the data.

For every solute-solvent system, the diffusion coefficient increases rapidly as temperature increases. At a constant temperature, the diffusion coefficient is larger 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 was observed for 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 Figures 7.1 to Figures 7.3 and Figure 7.2 to Figure 7.4. Octacosane is a larger and heavier molecule than eicosane. For this reason, at the same experimental conditions, diffusion coefficients for each solute are significantly smaller in the solvent n-octacosane than in n-eicosane.

Diffusion coefficients for alkane and gaseous solutes in the Fischer-Tropsch wax are plotted versus temperature in Figure 7.5 and 7.6. Diffusion coefficients for

Table 7.1 Infinite Dilution Diffusion Coefficients for Alkanes  
in n-Eicosane, n-Octacosane, and Fischer-Tropsch Wax  
( $D_{12}^{\infty} \times 10^9 \text{ m}^2/\text{s}$ ,  $\pm 1$  standard deviation)

T (K)	P (kPa)	C <sub>8</sub>	C <sub>10</sub>	C <sub>12</sub>	C <sub>14</sub>	C <sub>16</sub>
Solvent: n-Eicosane						
375	1380	1.85 ± 0.06	-	1.33 ± 0.01	-	1.06 ± 0.03
413	1410	2.86 ± 0.02	2.43 ± 0.01	2.13 ± 0.01	1.87 ± 0.03	1.68 ± 0.02
454	1400	4.22 ± 0.01	-	3.19 ± 0.01	-	2.56 ± 0.02
495	1380	6.09 ± 0.04	5.33 ± 0.02	4.65 ± 0.03	4.15 ± 0.02	3.75 ± 0.02
534	1320	8.34 ± 0.00	-	6.36 ± 0.06	-	5.08 ± 0.26
Solvent: n-Octacosane						
373	1430	1.22 ± 0.02	-	0.89 <sup>1</sup>	-	0.71 ± 0.01
413	1380	2.16 ± 0.01	-	1.56 ± 0.05	-	1.25 ± 0.01
454	1380	3.20 ± 0.09	-	2.37 ± 0.01	-	1.89 ± 0.02
495	1390	4.70 ± 0.07	-	3.59 ± 0.04	-	2.84 ± 0.10
534	1370	6.33 ± 0.08	-	4.82 ± 0.09	-	3.91 ± 0.04
Solvent: Fischer-Tropsch Wax						
475	1400	3.99 ± 0.07	-	2.88 ± 0.11	-	1.88 ± 0.12
504	1400	5.15 ± 0.06	-	3.69 ± 0.23	-	2.55 ± 0.08
536	1400	6.07 ± 1.15	-	4.86 ± 0.08	-	3.02 ± 0.13

1. This value represents a single measurement.

Table 7.2 Infinite Dilution Diffusion Coefficients for Gases  
in n-Eicosane, n-Octacosane, and Fischer-Tropsch Wax  
( $D_{12}^0 \times 10^9 \text{ m}^2/\text{sec}$ ,  $\pm 1$  standard deviation)

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

1. This value represents a single measurement.

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

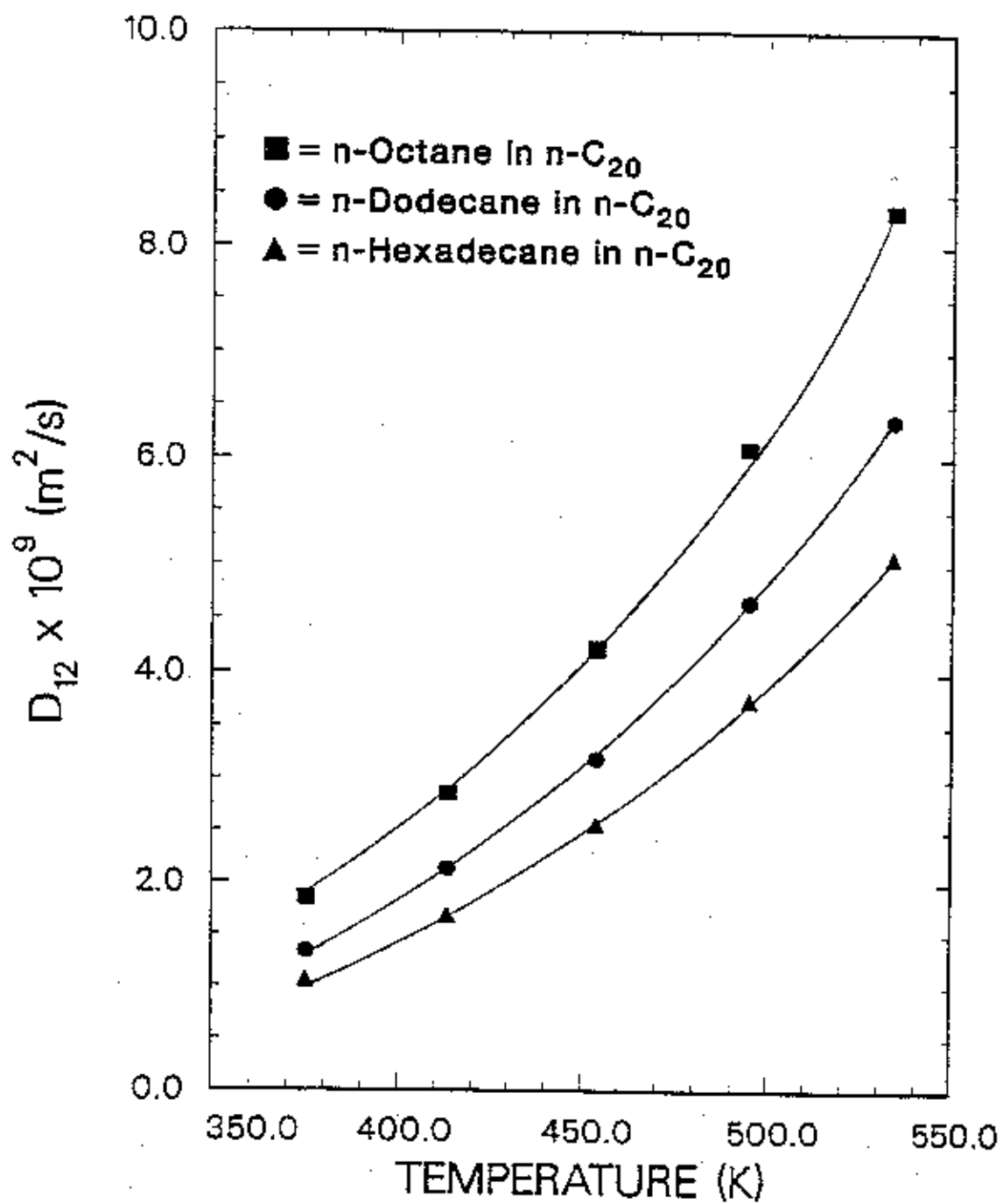


Figure 7.1. Diffusion coefficients for dilute n-alkanes in n-eicosane.

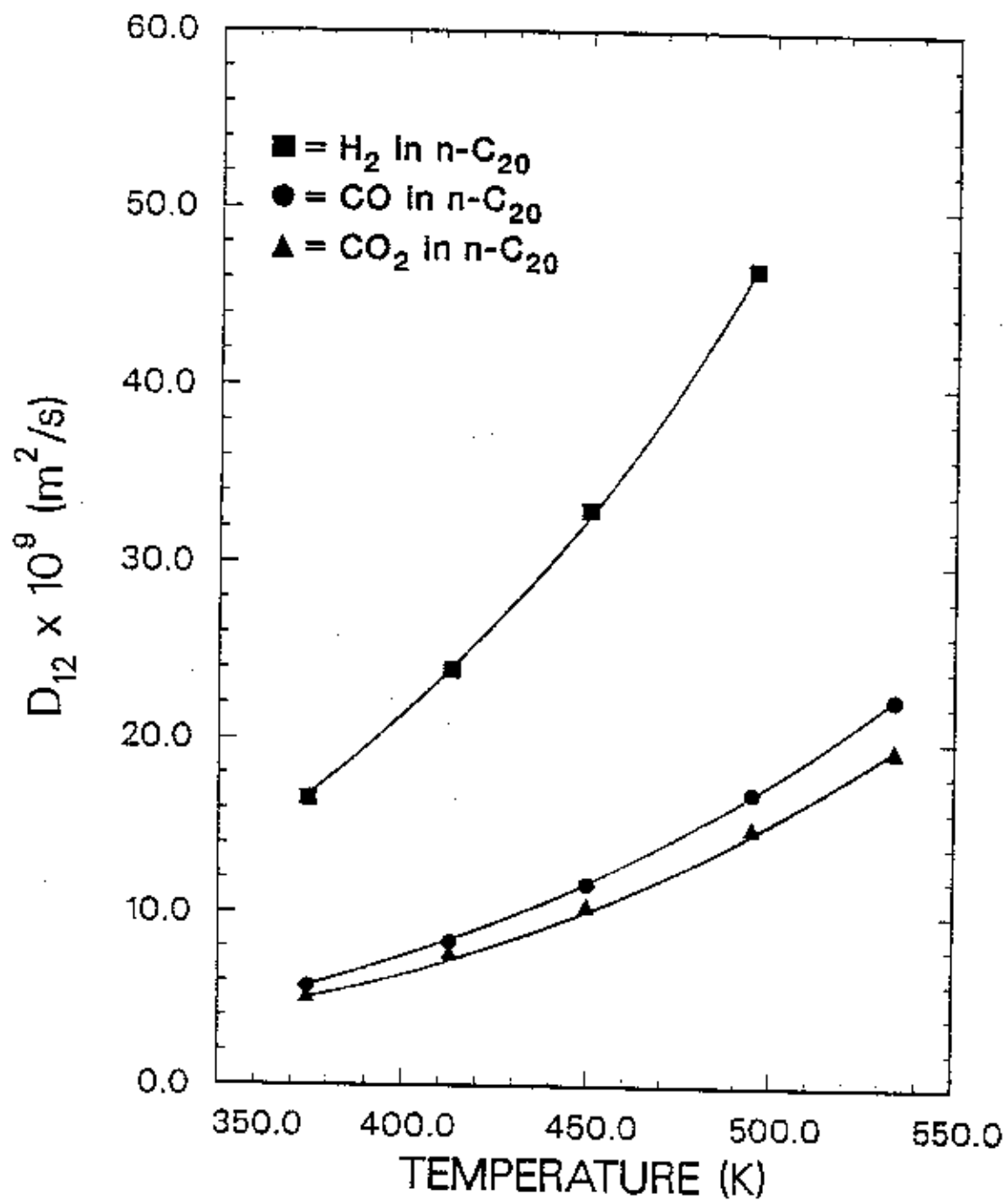


Figure 7.2. Diffusion coefficients for dilute gases in n-icosane.

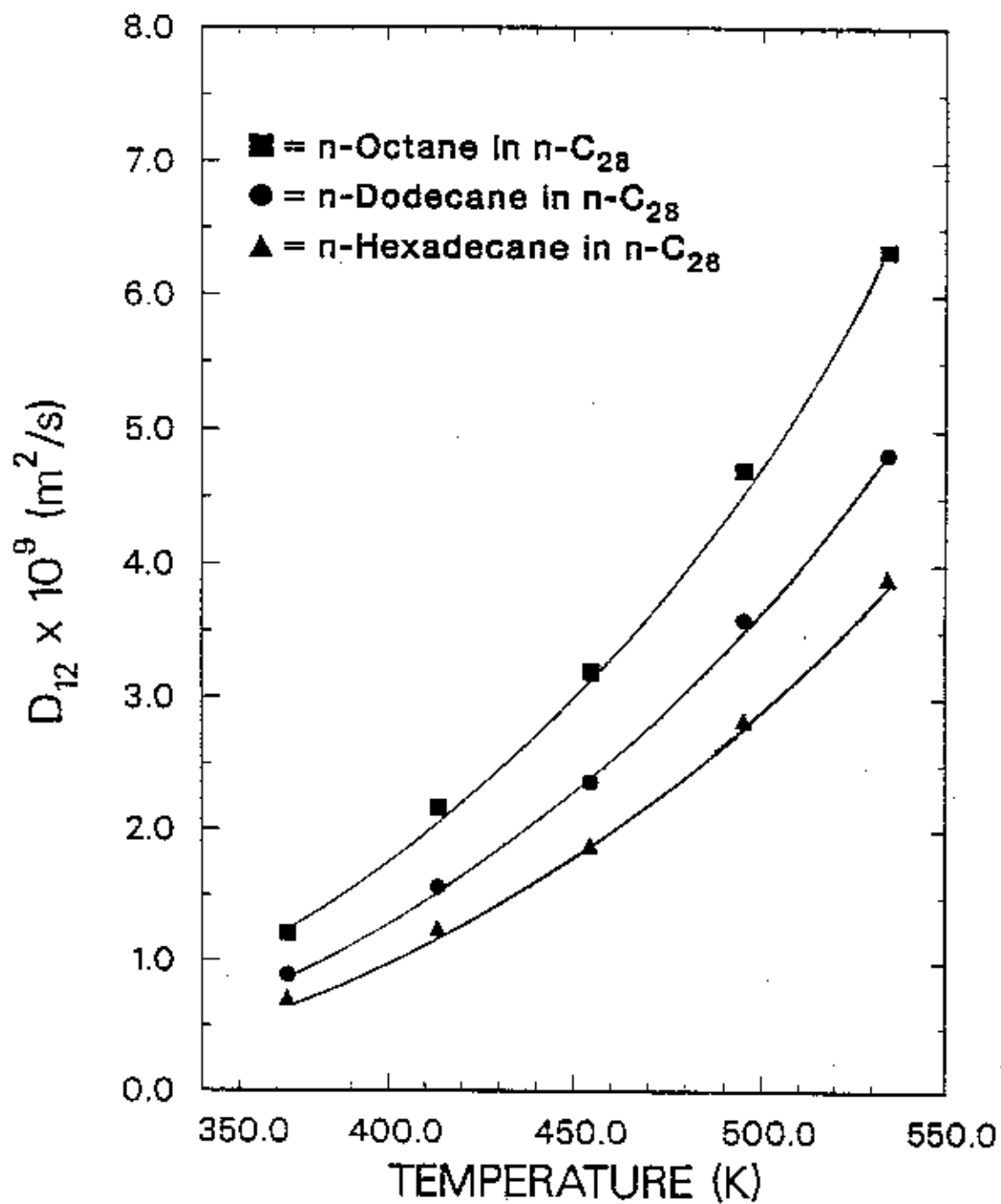


Figure 7.3. Diffusion coefficients for dilute n-alkanes in n-octacosane.

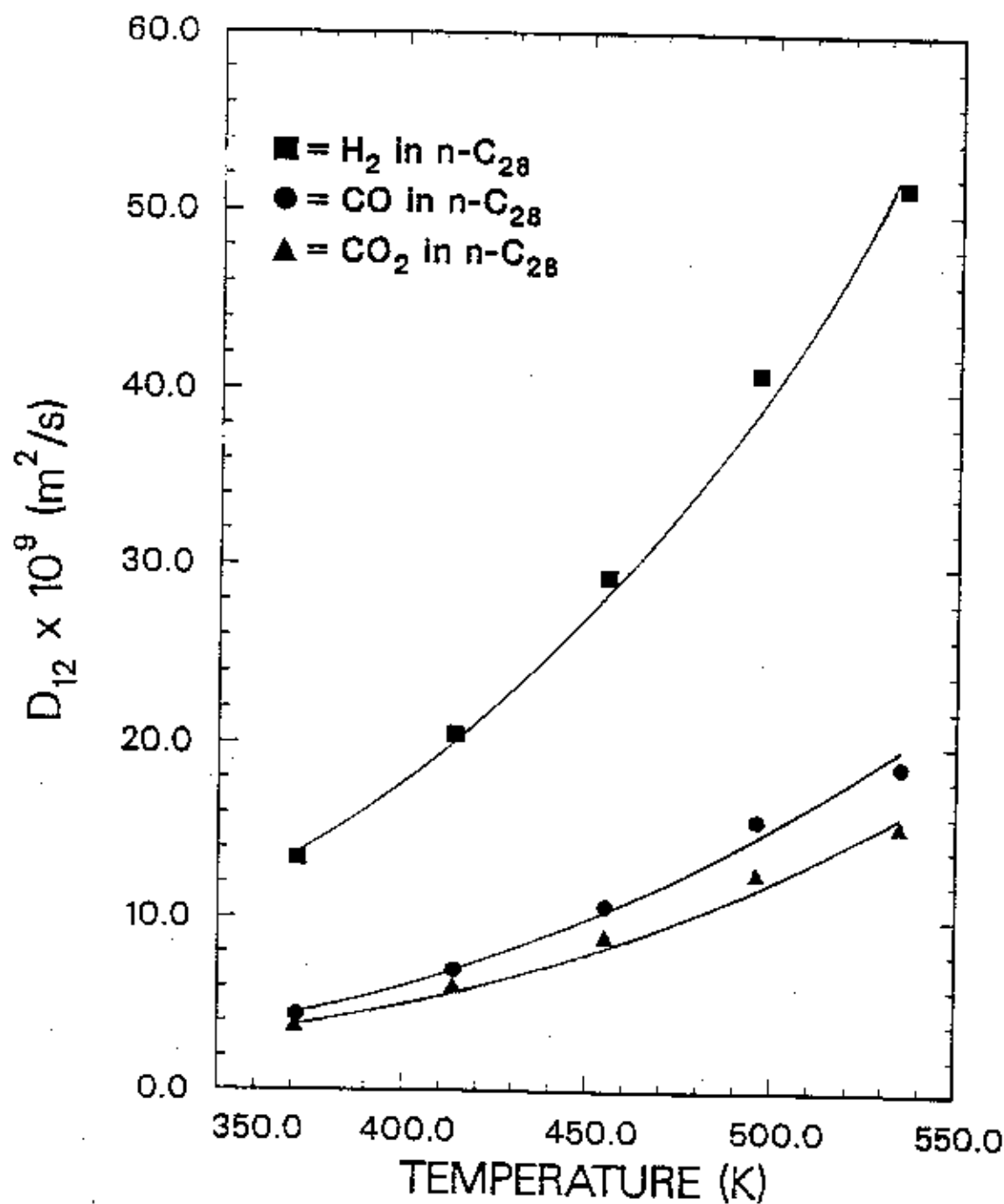


Figure 7.4. Diffusion coefficients for dilute gases in n-octacosane.



the same solutes in the solvent n-octacosane are also plotted in Figures 7.5 and 7.6. These plots illustrate that the diffusion coefficients measured in the Fischer-Tropsch wax data not only follow the same general trends as the n-octacosane data but agree closely in magnitude as well. This observation can be partially explained by the fact that the average carbon number of the FT wax was approximately 28, the carbon number of n-octacosane (see Chapter V). Later in this chapter, this result is discussed in detail.

The diffusion coefficient for hydrogen in the Fischer-Tropsch wax could not be measured at 536 K because the hydrogen completely reacted in the diffusion tube at this condition. Approximately 5 times the volume of a normal injection had to be injected in order to see a diffusion peak elute on the chart recorder. When enough hydrogen was injected to observe peaks, the peaks were greatly distorted, as if they may have contained a relatively high molecular weight product. Surprisingly, no unusual effects were noticed when diffusion coefficients were measured for hydrogen in FT wax at either 504 or 475 K.

It can only be surmised that either the FT wax contained catalyst fines, the stainless steel tube itself acted as a catalyst, or that certain high molecular weight compounds spontaneously became unstable at the highest experimental temperatures. Unfortunately, this problem could not be pursued without taking the risk of fouling the diffusion tube with the unknown reaction products.

Following the completion of the Fischer-Tropsch experiments, selected measurements were repeated in the solvent n-hexadecane at conditions where data had been measured previously by Matthews et al. (1987a). Both diffusion coefficients and solvent density results agreed within experimental error with measurements made prior to the Fischer-Tropsch experiments. These results confirmed that significant

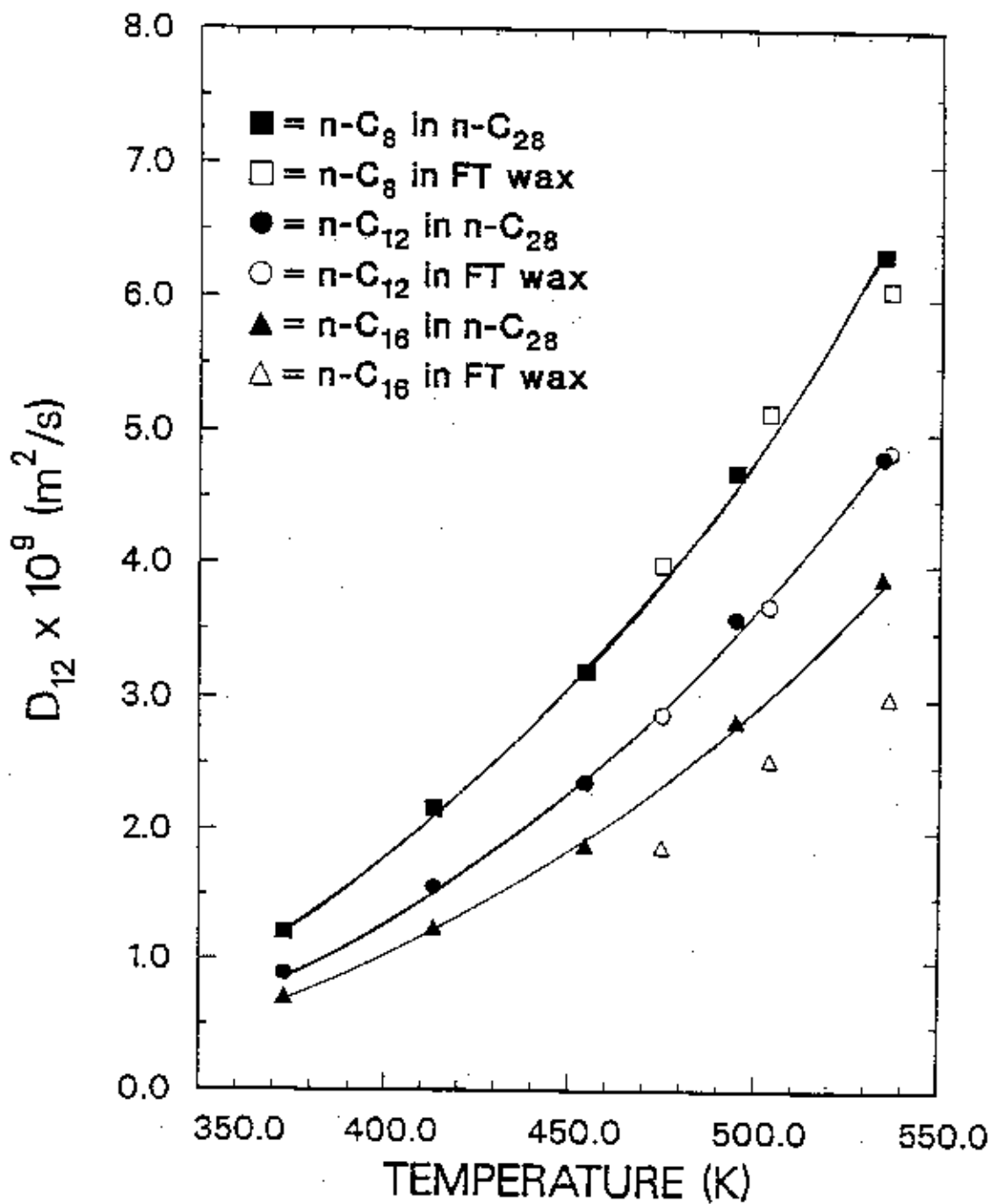


Figure 7.5. Diffusion coefficients for dilute n-alkanes in Fischer-Tropsch wax.

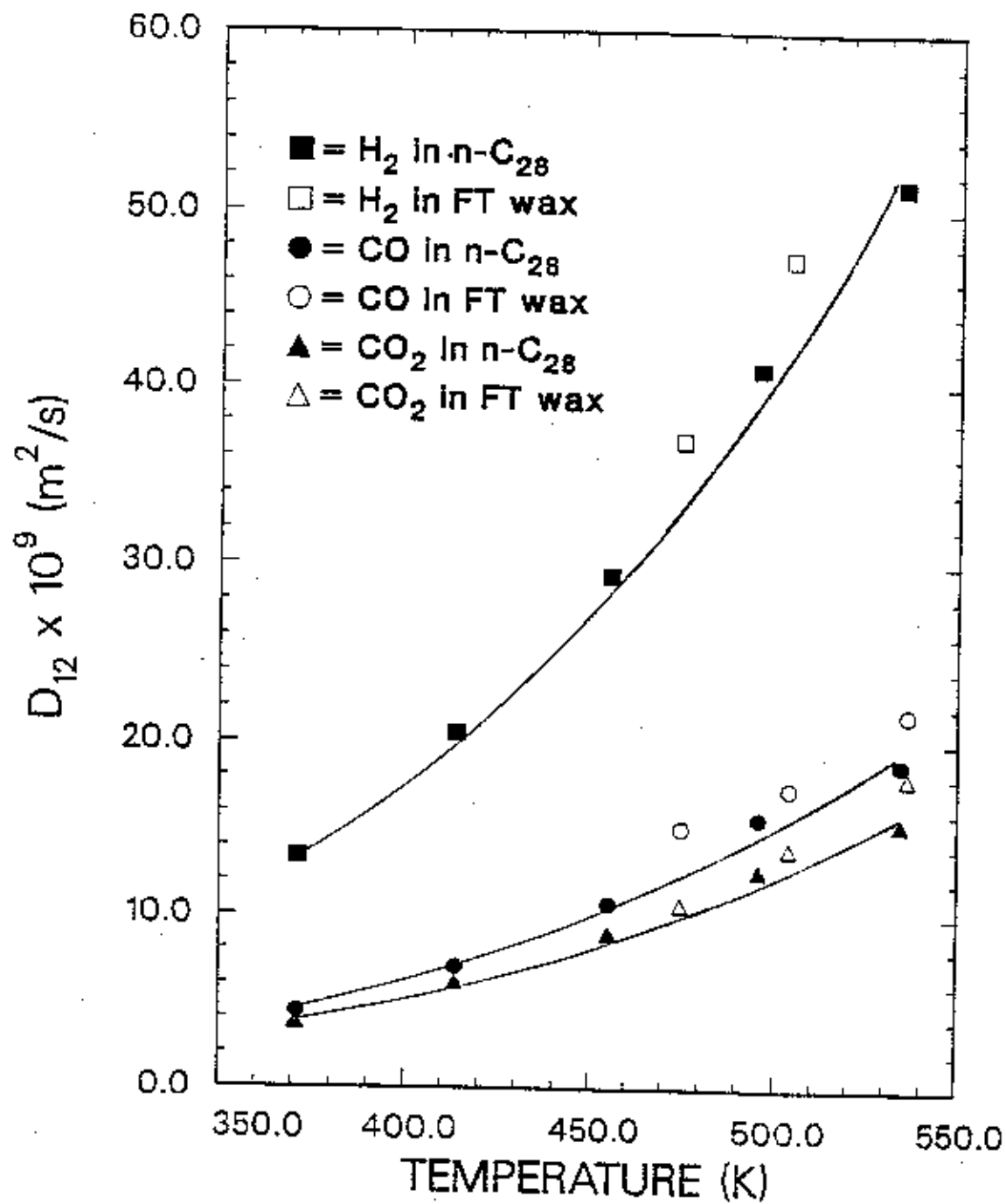


Figure 7.6. Diffusion coefficients for dilute gases in Fischer-Tropsch wax.

fouling of the diffusion tube had not occurred.

## B. CORRECTION OF PREVIOUSLY REPORTED VALUES

Diffusion coefficients reported from the first phase of the Texas A&M diffusion study (Matthews, 1986) were recalculated using the computer model which was described in Chapter VI. The corrected values of the diffusion coefficients for dilute  $n\text{-C}_8$ ,  $n\text{-C}_{10}$ ,  $n\text{-C}_{12}$ ,  $n\text{-C}_{14}$ , and  $n\text{-C}_{16}$  in the alkane solvents  $n\text{-C}_7$ ,  $n\text{-C}_{12}$ , and  $n\text{-C}_{16}$  are given in Table C.1 of Appendix C. The corrected values for hydrogen, carbon monoxide, and carbon dioxide in the same solvents are given in Table C.2 of Appendix C. The data cover the temperature range 298 to 566 K at pressures of approximately 1400 and 3450 kPa (200 and 500 psia).

The diffusion coefficients calculated by Matthews (1986) using the moment method generally agreed with the data in Appendix C to within 3 percent, but there were several severe exceptions. As expected (see Chapter VI), the agreement for the low temperature alkane data was poor, with some moment method results 7% higher than the results given in Appendix C.

Several diffusion coefficients for gaseous solutes calculated by the moment method were also in error by several percent. The largest errors were 10 - 12% and occurred for hydrogen solute peaks which are typically very narrow. Errors of this magnitude did not occur when the moment method was originally used to calculate the diffusion coefficients for gaseous solutes in  $n\text{-eicosane}$ , and  $n\text{-octacosane}$ . These errors can most likely be attributed to the fact that the moment method is highly susceptible to errors in the selection of the peak end points for such narrow peaks. This source of error has been eliminated by the new curve fitting procedure which has been demonstrated to be relatively insensitive to peak end point selection.

Table 7.3. Density of n-Eicosane, n-Octacosane, and Fischer-Tropsch Wax

T (K)	P <sub>this work</sub> (kPa)	$\rho$ this work (gm/cm <sup>3</sup> )	$\rho$ literature (gm/cm <sup>3</sup> )
Solvent: n-Eicosane			
375	1380	0.735	0.733 <sup>3</sup>
413	1410	0.712	0.709 <sup>3</sup>
454	1400	0.684	NA
495	1380	0.654	NA
534	1320	0.626	NA
Solvent: n-Octacosane			
373	1430	0.756	0.7555 <sup>4</sup>
413	1380	0.734	0.730 <sup>4</sup>
454	1380	0.705	0.703 <sup>4</sup>
495	1390	0.675	0.676 <sup>4</sup>
534	1370	0.651	0.650 <sup>4</sup>
Solvent: Fischer-Tropsch Wax			
454	1400	0.700 <sup>1</sup>	NA
475	1400	0.687	NA
495	1400	0.675 <sup>2</sup>	NA
504	1400	0.669	NA
534	1400	0.645 <sup>2</sup>	NA
536	1400	0.643	NA

1. Obtained from linear extrapolation of actual data.
2. Obtained from linear interpolation of actual data.
3. Texas A&M Thermodynamics Research Center Tables (1986, cf. API Research Project 44): atmospheric pressure.
4. Doolittle and Peterson (1951): measured with pycnometer, corrected to vacuum.

#### D. ROUGH HARD SPHERE CORRELATION

Although the relationship given by Equation 4.20 has been found to accurately predict measured infinite dilution diffusion coefficients for a wide variety of solutes diffusing in n-alkane systems (Matthews and Akgerman, 1987b; and Chen et al., 1982), a rigorous explanation of the equation in terms of Rough Hard Sphere parameters has never been given in the literature. Equation 4.20 is recalled below;

$$\frac{D_{12}^o}{\sqrt{T}} = \beta(V - V_D) \quad (4.20)$$

There is no theoretical justification for assuming that Equation 4.20 which is for mutual diffusion coefficients can be deduced from Equation 4.19. Equation 4.19 was developed by Dymond (1974) using self diffusion molecular dynamics machine calculations and was intended to apply only to self diffusion coefficients.

In order to understand the physical meaning of Equation 4.20, it is necessary to write the equation in terms of the Rough Hard Sphere parameters. This can be accomplished by starting with the general form of Equation 4.19, Dymond's (1974) equation for the RHS self diffusion coefficient. Following some algebraic manipulations, Equation 4.19 can be written in general as;

$$\frac{D^{DYM}}{\sqrt{T}} = A \cdot \frac{B}{m_2^{1/2} \sigma_2^2} \cdot (V - bV_o) \quad (7.1)$$

where  $D^{DYM}$  is the Dymond self diffusion coefficient, B is a universal constant for all fluids, and A is the translational-rotational coupling factor discussed in Chapter IV. An expression can then be written for  $D_{12}$  in terms of Dymonds self diffusion result;

$$D_{12} = \frac{D_{12}^{RHS}}{D_{22}^{RHS}} \cdot D^{DYM} \quad (7.2)$$

In Equation 7.2,  $D_{22}$  is the self diffusion coefficient of the solvent, 2.

When Equations 4.16 and 4.17 are substituted into Equation 7.2 for  $D_{22}^{RHS}$  and  $D_{12}^{RHS}$ , the equation for  $D_{12}$  becomes:

$$\frac{D_{12}^{\circ}}{\sqrt{T}} = \beta \cdot (V - bV_0) \quad (7.3)$$

where  $\beta$  is given by the following expression:

$$\beta = \frac{K}{\sigma_{12}^2} \left[ \frac{(m_1 + m_2)}{m_1 m_2} \right]^{1/2} \cdot A_{12} \frac{g(\sigma_{22})}{g(\sigma_{12})^{\circ}} \frac{[D_{12}^{SHS}/D_{12}^{CE}]_{MD}^{\circ}}{[D_{22}^{SHS}/D_{22}^{CE}]_{MD}} \quad (7.4)$$

In these equations,  $K$  is a universal constant. The superscript  $^{\circ}$ , which refers to the special case of infinite dilution, has been used because only infinite dilution diffusion coefficients were measured during this study and because only infinite dilution molecular dynamics data are available in the literature. However, the equation could be written in general and used to predict the concentration dependent mutual diffusion coefficient if molecular dynamics data were known as a function of solute concentration.

The parameter  $\beta$  in Equation 7.4 is a complicated function of  $\sigma_1$ ,  $\sigma_2$ ,  $m_1$ ,  $m_2$ ,  $I_1$ ,  $I_2$ , and  $V$ , but is constant for any given solute-solvent pair. Since there is not enough information available to calculate  $\beta$ , an alternative approach is to develop a correlation based on the parameters which are known or can easily be estimated. Of course, before such a correlation can be developed, it is necessary to demonstrate that the data fits the general form of the model.

In Figures 7.7 through 7.10,  $D_{12}/\sqrt{T}$  was plotted versus  $V$  for the same solute-solvent systems which were plotted in Figures 7.1 through 7.4. There was a strong linear relationship for each solute-solvent pair indicating that the parameter  $\beta$  does not depend strongly on the solvent molar volume,  $V$ . This linear behavior could not have been deduced from Equations 7.3 and 7.4 since the individual pair distribution functions and molecular dynamics terms are each strong functions of molar volume.

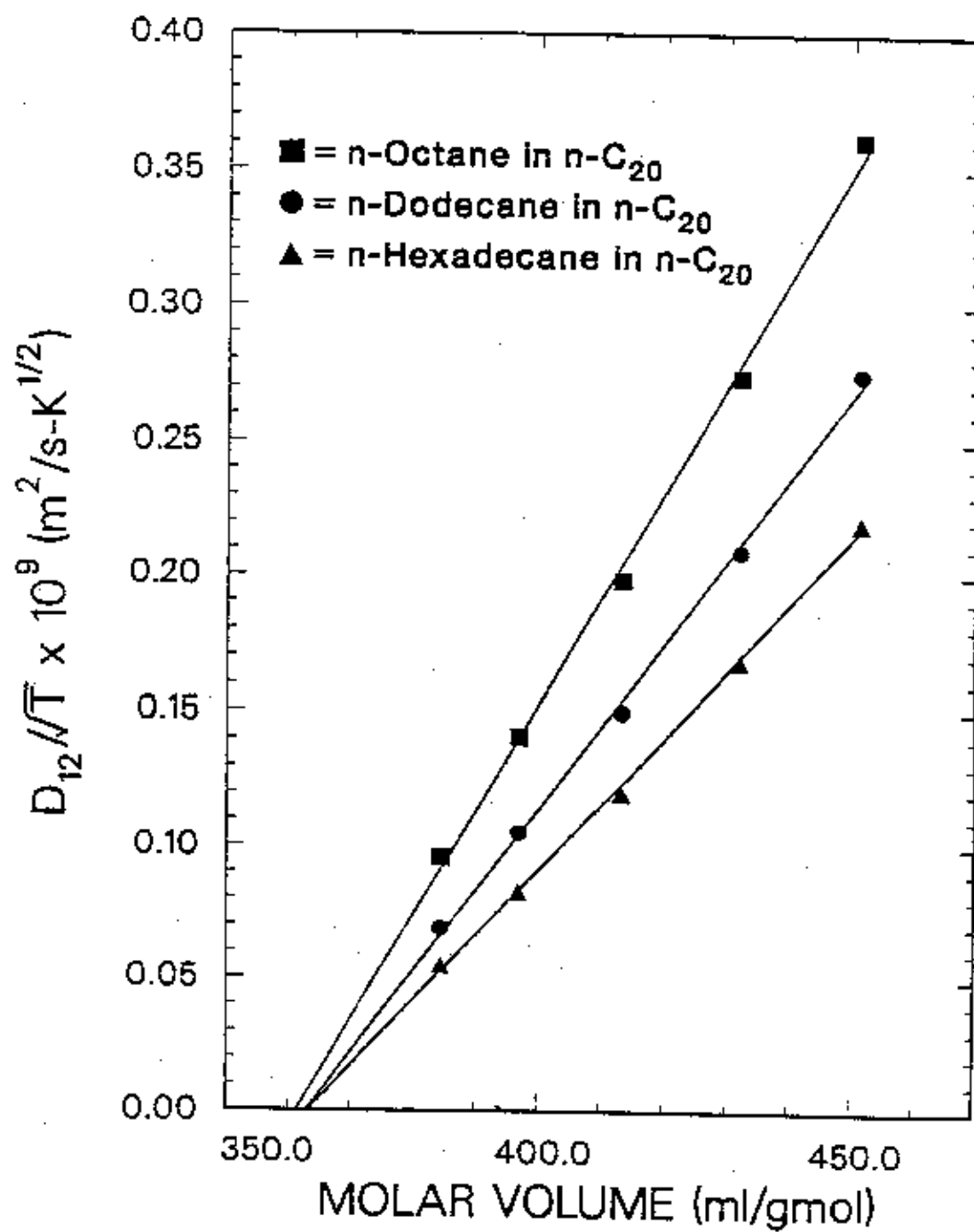


Figure 7.7. Linear behavior of  $D_{12}^0/\sqrt{T}$  versus  $V$  for n-alkane solutes in n-eicosane.



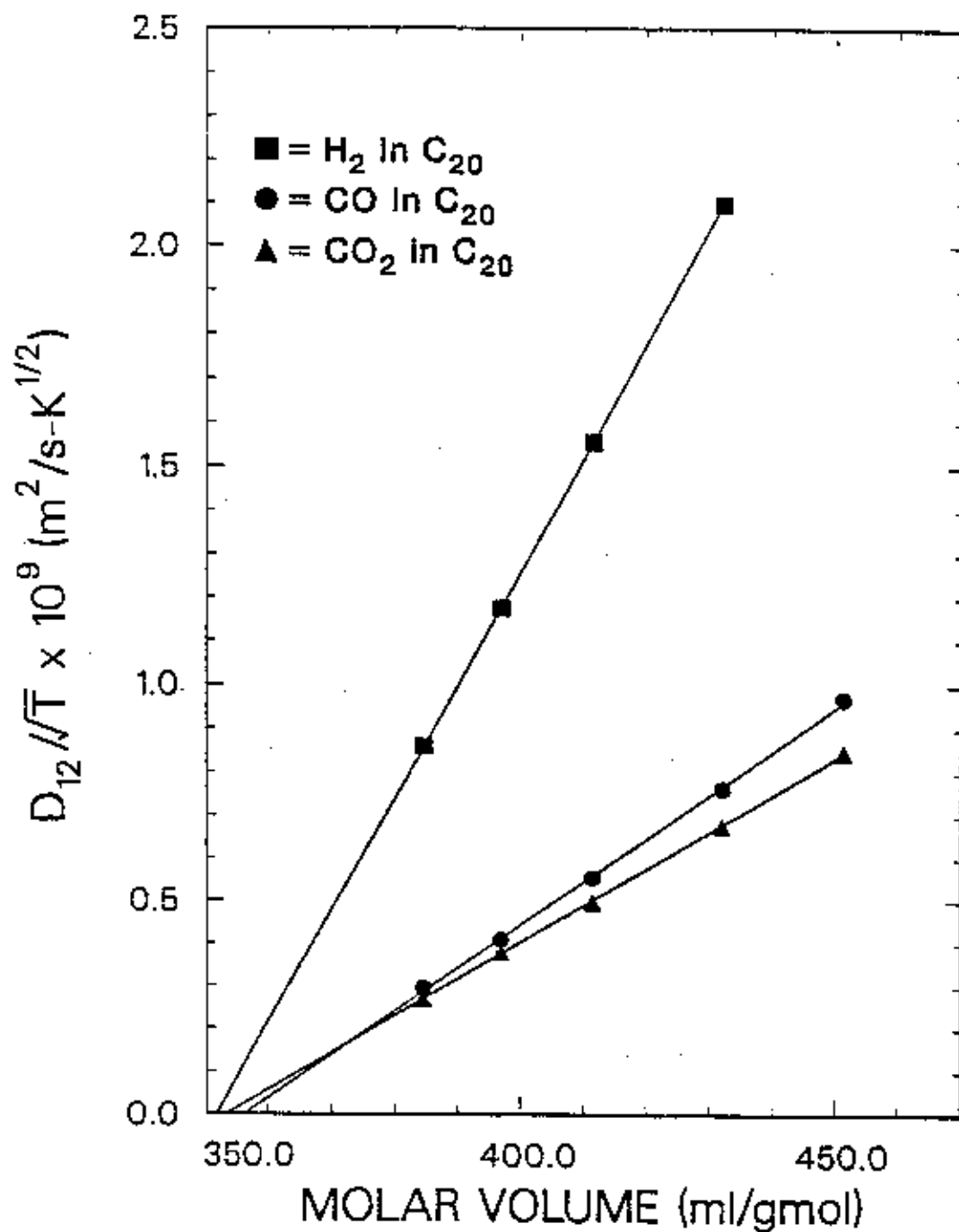


Figure 7.8. Linear behavior of  $D_{12}^0/\sqrt{T}$  versus  $V$  for gaseous solutes in n-eicosane.

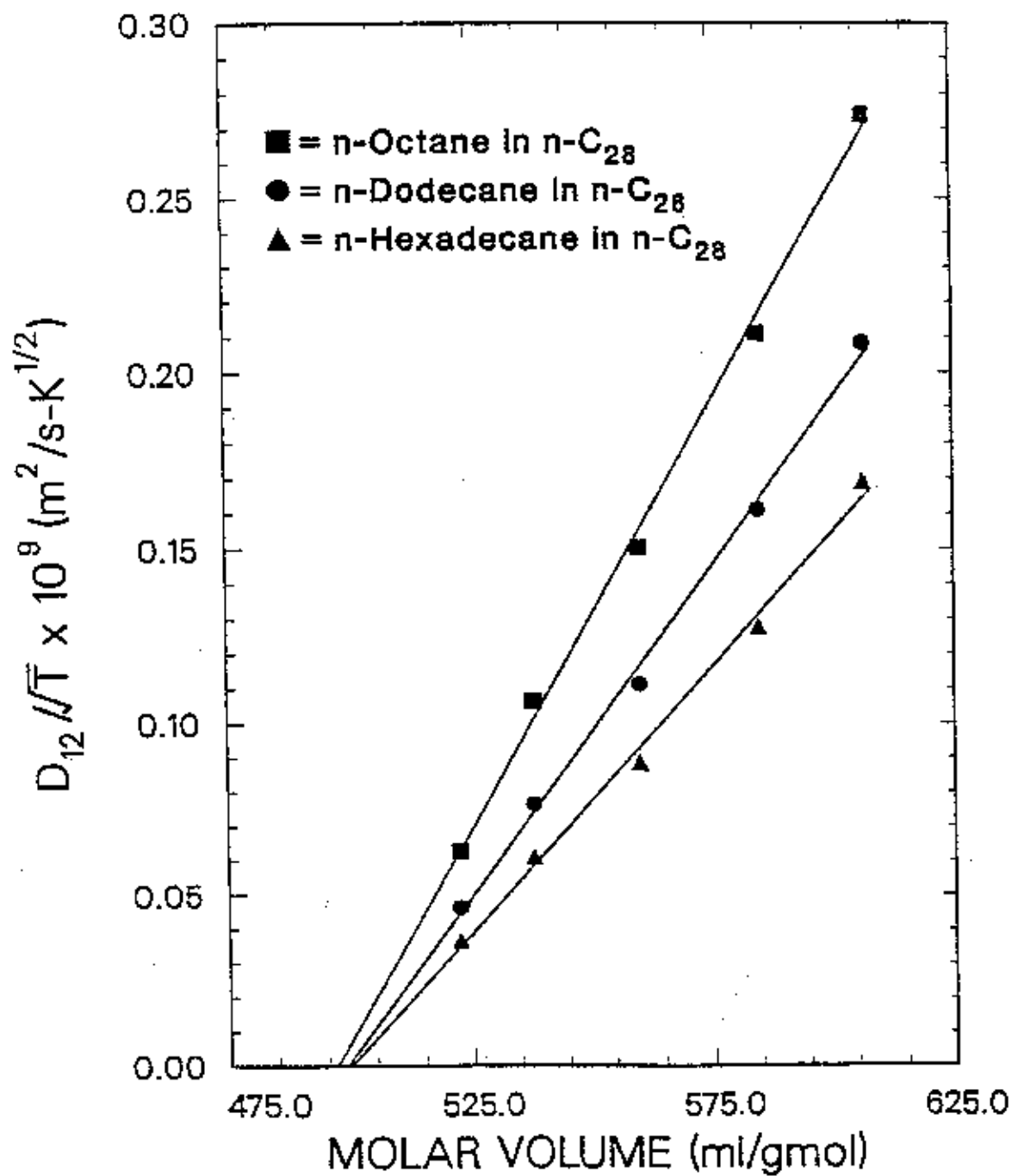


Figure 7.9. Linear behavior of  $D_{12}^0 / \sqrt{T}$  versus  $V$  for n-alkane solutes in n-octacosane.

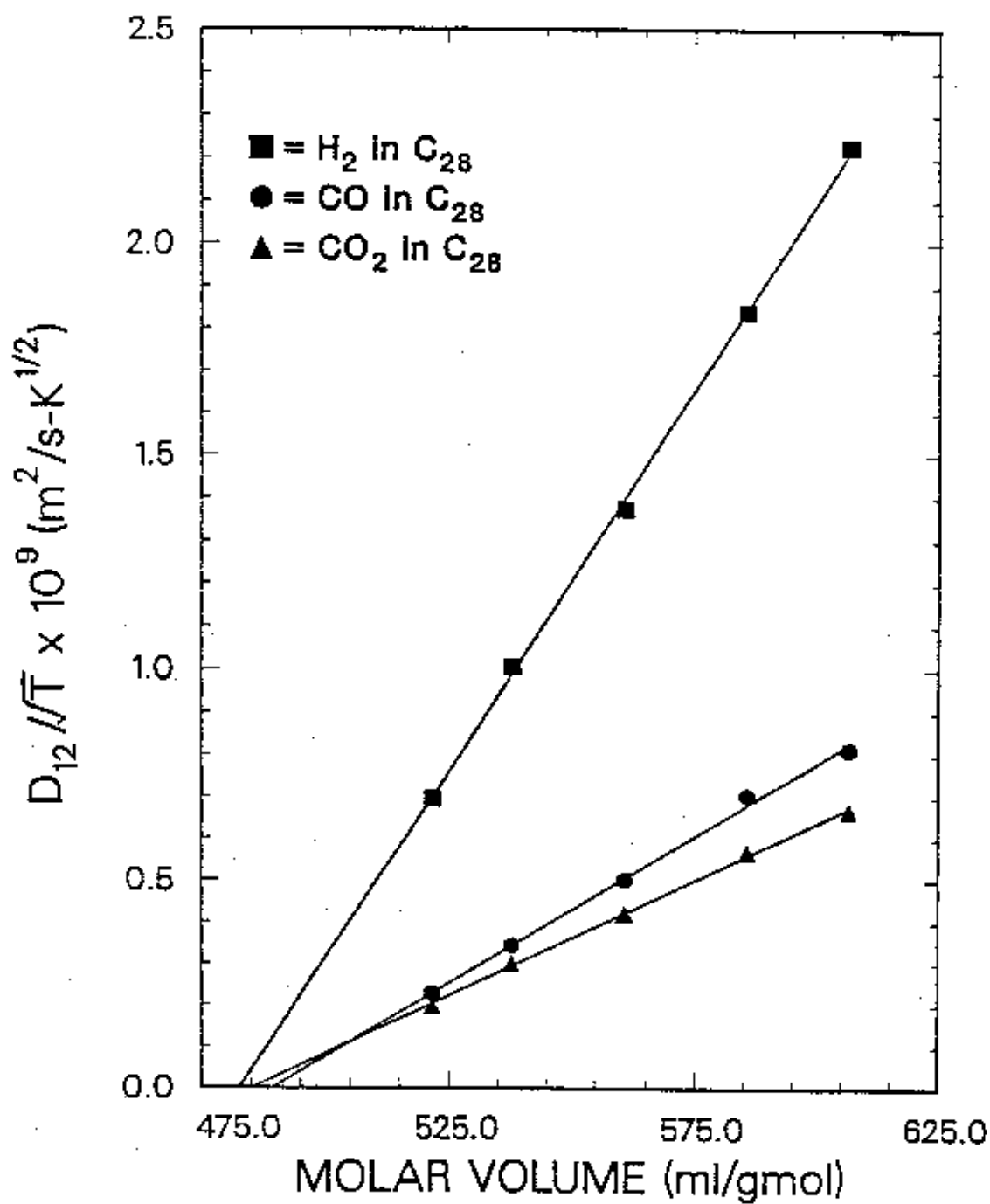


Figure 7.10. Linear behavior of  $D_{12}^0/\sqrt{T}$  versus  $V$  for gaseous solutes in n-octacosane.

Table 7.4 Linear Regression of  $D_{12}^0/\sqrt{T}$  versus Solvent Molar Volume for the Solvents n-Eicosane and n-Octacosane

$$10^9 D_{12}^0/\sqrt{T} = \beta(V - V_D)$$

( $D_{12}^0$  in  $\text{m}^2/\text{s}$ ,  $T$  in K,  $V$  in  $\text{cm}^3/\text{mol}$ )

Solute	$\beta$	$V_D$ ( $\text{cm}^3/\text{mol}$ )
Solvent: n-Eicosane		
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 <sub>2</sub>	0.02604	351.6
CO	0.01012	356.1
CO <sub>2</sub>	0.008629	353.2
Solvent: n-Octacosane		
n-octane	0.02445	496.5
n-dodecane	0.001901	498.7
n-hexadecane	0.001541	499.5
H <sub>2</sub>	0.01788	482.5
CO	0.007073	489.2
CO <sub>2</sub>	0.005572	484.9

Using simple linear regression, the slopes and intercepts,  $\beta$  and  $V_D$ , were calculated for each solute-solvent pair and are given in Table 7.4 for the solvents n-eicosane and n-octacosane. Table 7.5 is a similar table for the data in Appendix C, which also followed the general form of Equation 4.20.

The intercepts  $V_D$ , as determined from regression analysis, were a strong function of the solvent properties, as expected. However,  $V_D$  also depended weakly on the solute. The gaseous solutes, which are much smaller and lighter than the alkanes, always yielded intercepts which were consistently lower than the alkane intercepts, and hydrogen, the smallest solute, had the lowest intercept for nearly every solvent. For most solvents, the intercepts increased with solute size and weight even for the alkane solutes, although the trend was difficult to describe

Table 7.5 Linear Regression of  $D_{12}^0/\sqrt{T}$  versus Solvent Molar Volume for the Solvents n-Heptane, n-Dodecane, and n-Hexadecane

$$10^9 D_{12}^0/\sqrt{T} = \beta(V - V_D)$$

( $D_{12}^0$  in  $\text{m}^2/\text{s}$ ,  $T$  in K,  $V$  in  $\text{cm}^3/\text{mol}$ )

Solute	$\beta$	$V_D$ ( $\text{cm}^3/\text{mol}$ )
Solvent: n-Heptane		
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 <sub>2</sub>	0.06473	128.9
CO	0.02757	134.1
Solvent: n-Dodecane		
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 <sub>2</sub>	0.04301	215.8
CO	0.01637	215.4
CO <sub>2</sub>	0.01412	214.4
Solvent: n-Hexadecane		
n-octane	0.005351	290.4
n-decane	0.005139	293.3
n-dodecane	0.004120	289.5
H <sub>2</sub>	0.02928	281.2
CO	0.01259	284.7
CO <sub>2</sub>	0.01072	282.6

quantitatively because the intercepts were 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.

Equation 7.3 predicted that  $V_D$  is given by the following simple relationship, where  $b$  is a constant,  $N$  is Avogadro's number, and  $V_o$  is the theoretical close-

packed volume for solvent spheres of diameter  $\sigma_2$ ;

$$V_D = bV_0 = bN\sigma_2^3/\sqrt{2} \quad (7.5)$$

Although molecular dynamics data for self diffusion indicated that  $b$  was a constant, it was allowed to be a weak function of solute size for mutual diffusion in accordance with the trends observed in the experimental data. Values for  $\sigma$  were calculated using Bondi's (1964) group contribution method which was based on experimental x-ray diffraction data and are given in Table 7.6. (This table also includes the molecular weights of all solutes and solvents.) 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. Bondi's method was chosen because it allows the calculation of a consistent set of molecular diameters for several different groups of compounds. It would be preferable to use true hard sphere  $\sigma$ 's, but unfortunately the self diffusion and viscosity data which is necessary to calculate the hard sphere  $\sigma$ 's is not available for many compounds.

Using simple linear regression of the intercepts in Tables 7.4 and 7.5, the following simple formula was developed for  $b$ ;

$$b = 1.206 + 0.0632(\sigma_1/\sigma_2) \quad (7.6)$$

This formula reduces to the constant 1.269 for the case of self diffusion, where  $\sigma_1$  equals  $\sigma_2$ . With  $b$  equal to 1.269, Equation 7.6 agrees closely with the triple point volume for each solvent, as shown in Table 7.7. 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.

One of the primary goals of this study was to correlate the gas and alkane solute diffusion coefficients in a single correlation. In order to achieve this goal, a

Table 7.6 Molecular Diameters and Weights for All Solutes and Solvents

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

1. Molecular diameters for all molecules except hydrogen were calculated using Bondi's (1964) method. Bondi (1964) did not provide data for H<sub>2</sub>.

2. Lennard-Jones  $\sigma$  given by Hirschfelder, et al. (1954) as calculated from viscosity data. (Lennard-Jones  $\sigma$ 's calculated from viscosity data closely match Bondi (1964)  $\sigma$ 's for most molecules smaller than n-heptane where comparisons are possible).

Table 7.7 Comparison of Solvent Limiting Molar Volumes ( $\text{cm}^3/\text{gmol}$ )

Solvent	$V_D, \text{exp.}$	$1.269V_0$	$V_{tp, liq}$
n-C <sub>7</sub> H <sub>16</sub>	129 - 136	135	129.3 <sup>1</sup>
n-C <sub>12</sub> H <sub>26</sub>	214 - 225	222	221.2 <sup>1</sup>
n-C <sub>16</sub> H <sub>34</sub>	281 - 290	293	292.2 <sup>1</sup>
n-C <sub>20</sub> H <sub>42</sub>	352 - 363	363	363.7 <sup>1</sup>
n-C <sub>28</sub> H <sub>58</sub>	483 - 500	503	503.0 <sup>2</sup>

1. Texas A&M Thermodynamics Research Center Tables (1973, cf. API Research Project 44): atmospheric pressure.

2. Linearly extrapolated with carbon number from data for lower molecular weight n-alkanes.

general expression for the slopes,  $\beta$ , was necessary.  $\beta$  was allowed to be a function of only the following RHS parameters;  $\sigma_1$ ,  $\sigma_2$ ,  $M_1$ , and  $M_2$ .  $\beta$  was not allowed to be a function of  $V$ , because Figures 7.7 through 7.10 indicated that the dependence of  $D_{12}/\sqrt{T}$  on  $V$  was adequately described by the term  $(V - bV_0)$ . The moments of inertia  $I_1$  and  $I_2$ , which are functions of the individual bond lengths and atomic masses, were not included as parameters in the correlation for  $\beta$ , because these parameters cannot be easily calculated except for the simplest of molecules.

Several representations were initially determined for  $\beta$  using linear regression which adequately correlated the diffusion of either gaseous or liquid n-alkane solutes in n-alkane solvents. However, none of these initial expressions adequately predicted diffusion coefficients for both gaseous and liquid solutes. Eventually an expression was developed which represented all of the data using only the following four variables; the solute molecular weight,  $M_1$ ; the solvent molecular weight,  $M_2$ ; the



solute diameter,  $\sigma_1$ ; and the solvent diameter,  $\sigma_2$ . The functional form found to represent the slopes,  $\beta$ , is given by the following equation;

$$\beta = \frac{a}{M_1^b M_2^c (\sigma_1 \sigma_2)^d} \quad (7.7)$$

Using the form of the slope given in Equation 7.7, the following equation was developed which summarizes all of the diffusion coefficients in n-alkane solvents which were measured during this study, and also the previously measured diffusion coefficients which were given in Appendix C;

$$\frac{10^9 D_{12}^0}{\sqrt{T}} = \frac{94.5}{M_1^{0.239} M_2^{0.781} (\sigma_1 \sigma_2)^{1.134}} (V - bV_0) \quad (7.8)$$

In this equation,  $D_{12}$  is in  $\text{m}^2/\text{s}$ ,  $T$  is in Kelvin, molecular weights are in gm/mol, and the molar volumes are in  $\text{cm}^3/\text{mol}$ .  $V_0$  and  $b$  are given by Equations 7.5 and 7.6. The diameters  $\sigma_1$  and  $\sigma_2$  are in Angstroms and were given previously in Table 7.6 as calculated by the method of Bondi (1964).

Equation 7.8 predicts the data very well as illustrated by Figures 7.11 and 7.12. The average absolute percent deviation from the experimental data was 6.3%. The largest percentage errors occurred for alkane solutes at low temperatures where the absolute value of the diffusion coefficients were quite low. In such cases, the magnitude 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 7.8. In any given solvent, the equation predicts larger diffusion coefficients for 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.

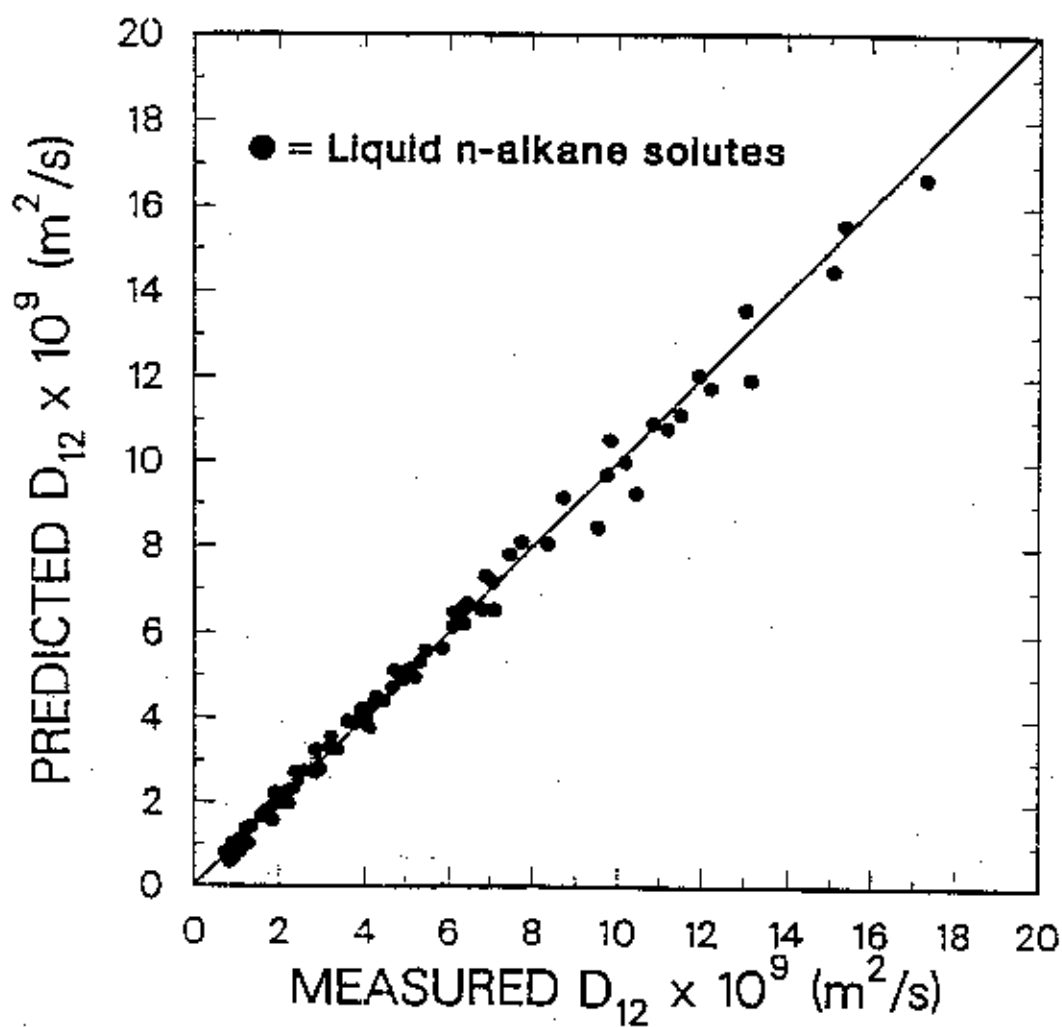


Figure 7.11. Comparison of measured diffusion coefficients for liquid n-alkane solutes in n-alkane solvents to the predictions of Equation 7.8.

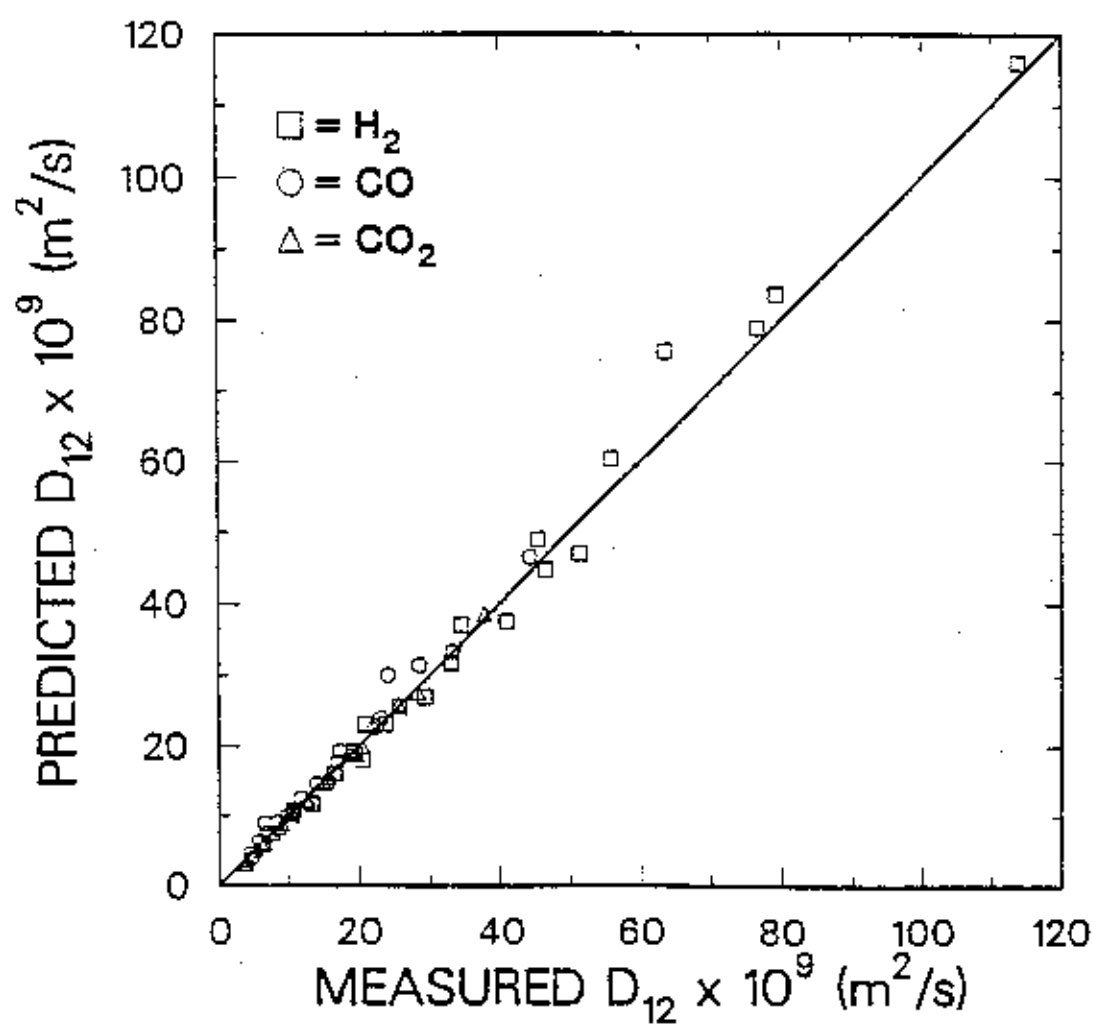


Figure 7.12. Comparison of measured diffusion coefficients for gaseous solutes in n-alkane solvents to the predictions of Equation 7.8.

In order to test the agreement of Equation 7.8 with the RHS theory, the equation was reduced to the following form for self diffusion;

$$\frac{10^9 D_{22}}{\sqrt{T}} = \frac{49.6}{M^{1.020} V_o^{0.758}} (V - 1.269 V_o) \quad (7.9)$$

The general form of Equation 7.9 is identical to the form of Equation 4.19 which was developed by Dymond (1974) using computer calculations for self diffusion. The fact that these equations are similar is a further indication that Equation 7.9 has a strong fundamental basis. From Equations 4.19 and 7.8, it can be shown that the translational - rotational coupling constant for self diffusion,  $A$ , for n-alkanes is approximately proportional to the following function of molecular weight;

$$A \propto \frac{1}{M^{0.6}} \quad (7.10)$$

$V_o$  has been eliminated from the above expression by employing the observation that  $V_o$  is approximately proportional to  $M$  for n-alkanes. An exact expression for  $A$  cannot be written because Bondi's (1974)  $\sigma$ 's do not agree exactly with hard sphere  $\sigma$ 's.

#### E. VALIDATION OF CORRELATION USING LITERATURE DATA

Equation 7.8 was tested using normal alkane-alkane infinite dilution mutual diffusion coefficient data from sixteen different literature sources. Solute carbon numbers ranged from 1 to 32 and solvent carbon numbers ranged from 6 to 16. The results of this comparison are given in Appendix D. Of 149 individual data points located in the literature, only 21 measurements were at temperatures above 50°C. In general, the agreement was excellent considering that Equation 7.8 was based on data almost exclusively measured above 50°C and was not intended for use at ambient conditions.

The correlation predicted the Taylor dispersion data of Alizadeh and Wakeham (1982) especially well. For this data set, which included 33 measurements in the solvents n-hexane, n-heptane, and n-octane, the average absolute percentage error was only 5.1%.

Equation 7.8 did not accurately predict the data of Moore and Wellek (1974) for the solute decane in solvents ranging from hexane to dodecane. For this particular data, which included 19 measurements, the predicted diffusion coefficients were consistently less than the measured values by an average of 27%. The large disparity between predicted and measured values was puzzling, until the data was compared to other data in the literature. Moore and Wellek's reported diffusion coefficients for the solute n-decane are consistently larger in magnitude than the data reported by others. Although several examples of disagreement can be noted, the most startling is for n-C<sub>10</sub> in n-C<sub>6</sub> at 25°C. Moore and Wellek (1974) reported  $D_{12}^o$  to be  $4.632 \times 10^{-9}$  m<sup>2</sup>/s while Bidlack et al. (1969) reported  $3.02 \times 10^{-9}$ . For n-C<sub>10</sub> in n-C<sub>7</sub> at 25°C, Moore and Wellek reported  $3.08 \times 10^{-9}$  while Lo (1974) reported  $2.54 \times 10^{-9}$ . Moore and Wellek's (1974) data was measured using a unique unsteady state porous frit apparatus which required a tedious calibration. Most likely the required calibration was in error.

The correlation given by Equation 7.8 consistently over predicted the methane solute data of Chen et al. (1982) by an average of 28% for 14 datapoints. A portion of this error may be due to the fact that Chen's diffusion coefficients were calculated using the graphical analysis method for Taylor dispersion (see Chapter II). However, it is unlikely that the sole source of error can be explained by the data analysis method. It may be difficult for the model to accurately predict diffusion for small gaseous solutes because n-C<sub>8</sub> was the smallest alkane solute in the data

base which was used in the model development.

The correlation given by Equation 7.8 was also used to predict the diffusion coefficients measured by Chen et al. (1982) for the noble gases argon, krypton and xenon in n-C<sub>8</sub>, n-C<sub>10</sub>, and n-C<sub>14</sub>, at temperatures of 298-433 K. Since Bondi (1974) did not give the necessary information to calculate molecular diameters for the noble gases, values of Lennard-Jones  $\sigma$ 's determined from viscosity data (Hirschfelder et al. (1954)) were used in Equation 7.8. These diameters were chosen because Lennard-Jones  $\sigma$ 's calculated from viscosity data closely match molecular diameters determined by Bondi's method where comparisons are possible. Equation 7.8 predicted the data for the noble gases extremely well as illustrated by Figure 7.13. For a total of 34 reported measurements, the correlation predicted the results with an average absolute error of 12.8%. Since Chen et al. (1982) calculated the reported diffusion coefficients using the graphical method of Taylor dispersion analysis, a portion of the error between the predicted and observed results may be due to systematic error caused by the graphical method (see Chapter II).

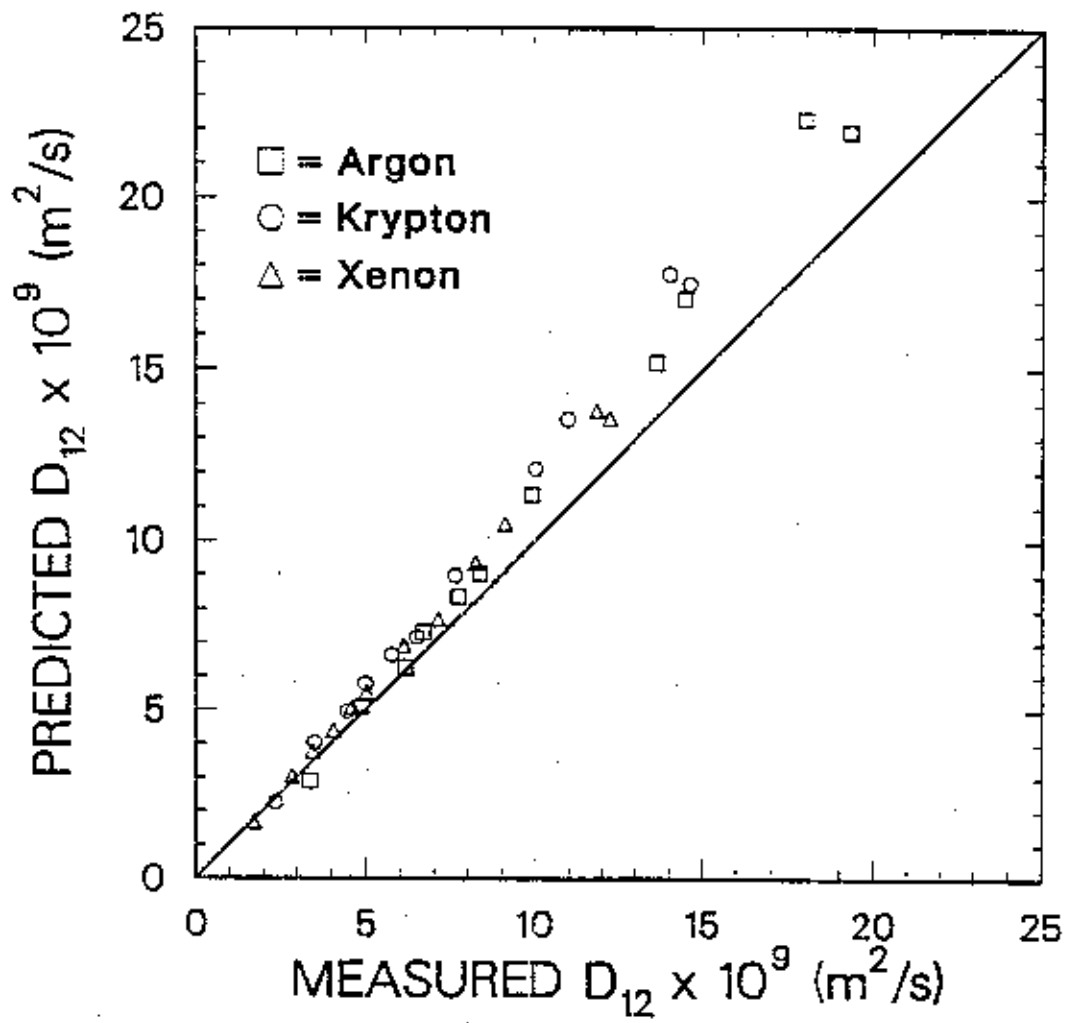


Figure 7.13. Comparison of measured diffusion coefficients for noble gases in n-alkanes (Chen et al., 1982) to predictions of Equation 7.8.

## F. PREDICTING DIFFUSION COEFFICIENTS IN FISCHER-TROPSCH WAX

Suggestions will now be given as to how Equation 7.8 may be used to predict diffusion coefficients in Fischer-Tropsch reactor wax. It has already been 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. The diffusion coefficients and densities measured in the Fischer-Tropsch wax were also demonstrated to be similar in magnitude to the corresponding measurements in n-octacosane, which also has a carbon number of 28. For estimation purposes, it is recommended that Equation 7.8 be used by treating the wax as a pure alkane with carbon number equal to the approximate average carbon number of the mixture. This suggested treatment is not based solely 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 modeling chain molecules using average chain length (Prigogine et al., 1953 and Longuet-Higgins (1953)).

The errors associated with using the suggested method decrease as the average carbon number increases. This point is illustrated by Figure 7.14 which shows the diffusion coefficients for n-alkane solutes as a function of n-alkane solvent carbon number at the constant temperature of 475 K, as predicted by Equation 7.8. An analogous plot for gaseous solutes is given in Figure 7.15. Both Figure 7.14 and Figure 7.15 illustrate that as solvent 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. The suggested method is bound to raise some concern regarding



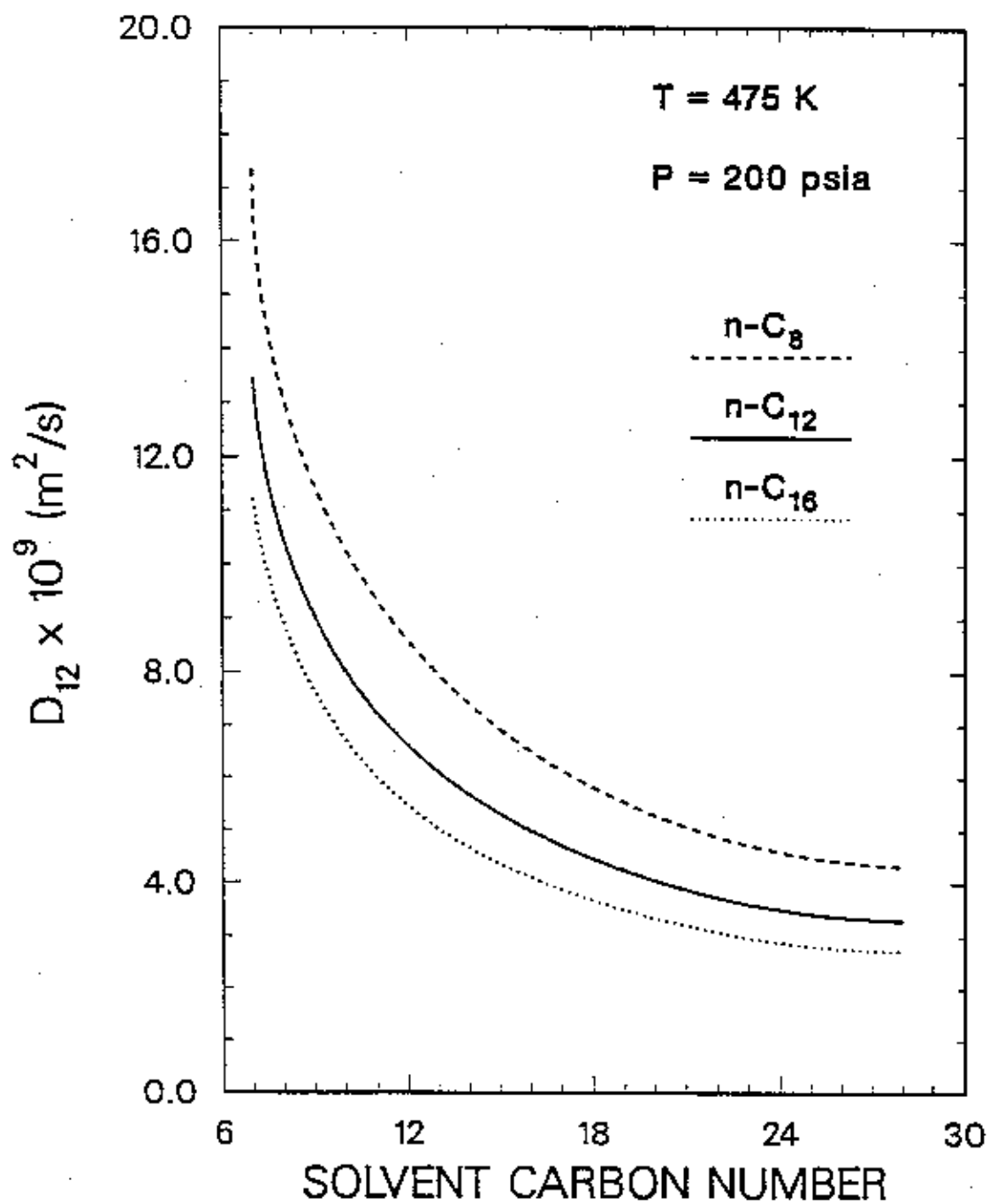


Figure 7.14. Effect of n-alkane solvent carbon number on the diffusion coefficients of dilute n-alkane solutes.

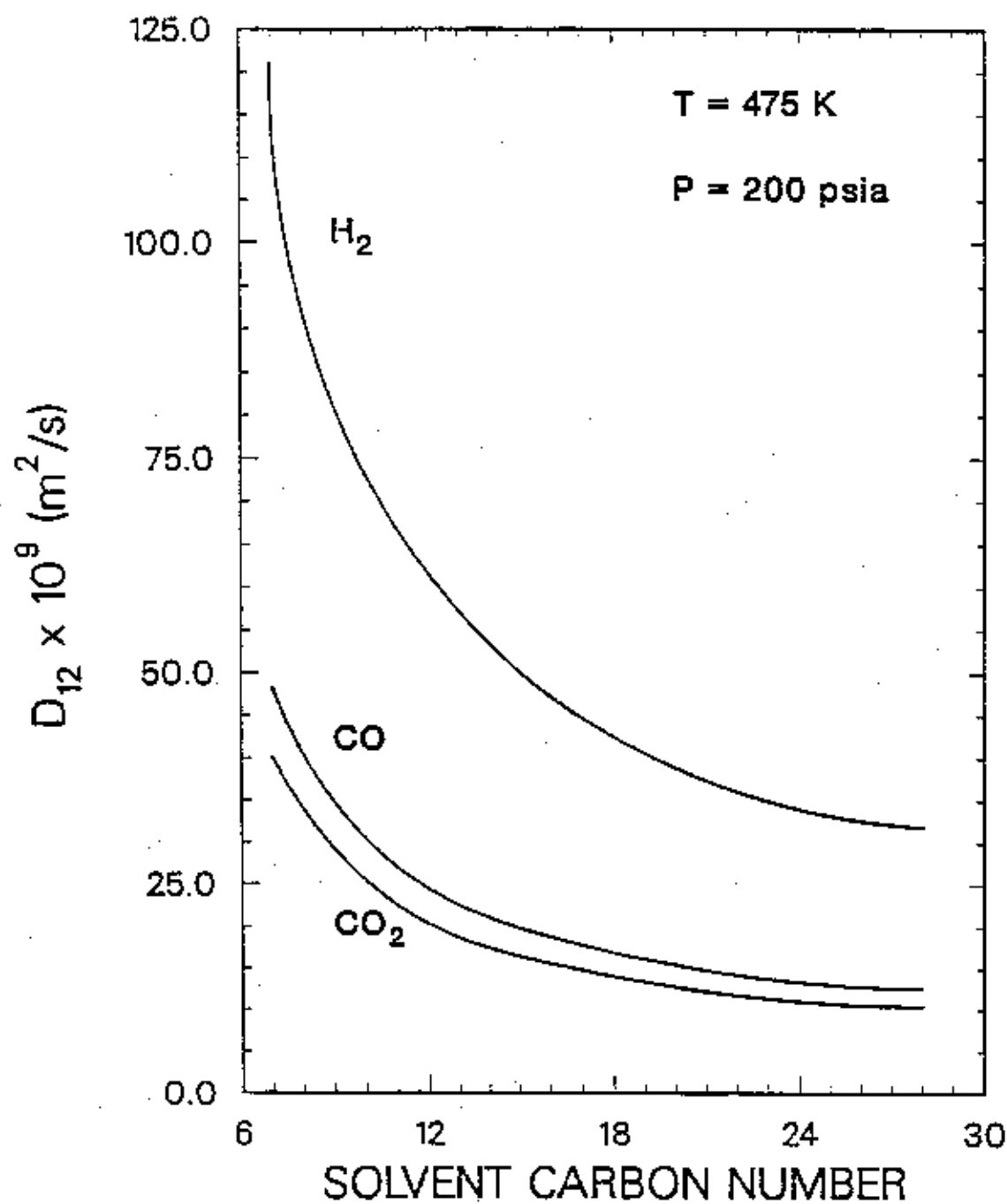


Figure 7.15. Effect of n-alkane solvent carbon number on the diffusion coefficients of dilute gaseous solutes.

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. The reason that the olefins in the sample did not affect the measured diffusion coefficients to a greater degree in this study 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 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.

The experimental data and suggested predictive scheme for diffusion coefficients in FT wax indicate that currently used estimates of diffusion coefficients in the wax are highly erroneous. The diffusion coefficient of hydrogen in Krupp wax was predicted by Satterfield and Huff (1980). Krupp wax is a refined Fischer-Tropsch paraffin typically used in FT reactors at the U.S. Bureau of Mines, U.K. Fuel Research Station and Rheinpreussen, Germany (see Satterfield and Huff (1980)) and has been adopted by many experimentalists as a standard Fischer-Tropsch wax. The properties of Krupp wax are closely approximated by the properties of n-triacontane ( $C_{30}$ ). Satterfield and Huff (1980) used the Wilke-Chang equation to predict the diffusion coefficient of the solute hydrogen in the solvent n-triacontane. The Wilke-Chang predictions were then correlated and the resulting correlation was

suggested by Satterfield and Huff (1980) for predicting the diffusion coefficient of hydrogen in Fischer-Tropsch wax:

$$D_{12} = 7.35 \times 10^{-7} \exp\left(\frac{-2285}{T}\right) \quad (7.11)$$

where  $D_{12}$  is in  $\text{m}^2/\text{s}$  and  $T$  is in K.

Kuo (1983) modeled an FT slurry reactor using the following correlations for gaseous solute diffusion coefficients in FT wax;

$$\text{For } \text{H}_2; \quad D_{12} = 3.90 \times 10^{-6} \exp\left(\frac{-2877}{T}\right) \quad (7.12a)$$

$$\text{For } \text{CO}; \quad D_{12} = 5.99 \times 10^{-8} \exp\left(\frac{-1633}{T}\right) \quad (7.12b)$$

$$\text{For } \text{CO}_2; \quad D_{12} = 3.70 \times 10^{-8} \exp\left(\frac{-1437}{T}\right) \quad (7.12c)$$

In these equations,  $T$  is the temperature in K, and  $D_{12}$  is the diffusion coefficient in  $\text{m}^2/\text{s}$ . Equation 7.12a was reported to be an extrapolation of the diffusion coefficients for hydrogen in Fischer-Tropsch wax measured by Peter and Weinert (1956). Equation 7.12b for carbon monoxide was developed to predict values of the diffusion coefficient which in turn could be used in mass transfer coefficient correlations to match experimental mass transfer coefficients. Equation 7.12c was an extrapolation of the diffusion coefficients for carbon dioxide in n-hexadecane at 25 and 50°C measured by Hayduk and Cheng (1971). Table 7.8 illustrates the dangers of such extrapolations by comparing the predictions of Equations 7.11, and 7.12 (a, b, and c) to the actual data measured in this study. The predictions of Equation 7.8, calculated by modeling the wax as n-C<sub>28</sub>, are also included for comparison.

Peter and Weinert (1956) actually measured the diffusion coefficient of hydrogen in a FT paraffin wax with a mean molecular weight of 340 to be approximately

Table 7.8. Comparison of FT Wax Diffusion Correlation Predictions to Measured Diffusion Coefficients  
( $10^9 D_{12}^0$ ,  $m^2/sec$ )

$T$ (K)	Solute	Measured <sup>1</sup>	Eq. 7.8 <sup>2</sup>	Eq.'s 7.12 <sup>3</sup>	Eq. 7.11 <sup>4</sup>
475	H <sub>2</sub>	36.9	31.9	9.13	5.99
504	H <sub>2</sub>	47.3	39.4	12.9	7.89
536	H <sub>2</sub>	NA	47.5	18.2	10.3
475	CO	15.1	12.6	1.92	NA
504	CO	17.4	15.6	2.35	NA
536	CO	21.7	18.9	2.85	NA
475	CO <sub>2</sub>	10.7	10.5	1.80	NA
534	CO <sub>2</sub>	14.0	13.0	2.14	NA
536	CO <sub>2</sub>	18.1	15.7	2.53	NA

1. Measured this work, see Table 7.2.
2. Developed this work.
3. Kuo (1983).
4. Satterfield and Huff (1980).

$60 \times 10^{-9} m^2/s$  at 200 psia and 473 K. Peter and Weinert's (1956) measurements depended on accurate estimates of hydrogen solubility and are therefore unlikely to be as dependable as the measurements reported in this study. However, even though the measurement of Peter and Weinert (1956) at 473 K and 200 psia, is considerably higher than would be indicated by the present study, it is much more reasonable than the predictions of either Equation 7.11 or Equation 7.12a.

Equation 7.11, which was based on the predictions of the Wilke-Chang equation, failed because hydrodynamic models such as the Wilke-Chang equation cannot be expected to accurately predict diffusion coefficients in dilute solutions when the solute molecule is much smaller than the solvent molecule (see Chapter IV). The reason for the large discrepancy between the predictions of Equation 7.12a and the measured results is unclear considering the fact that Kuo (1983) reported Equation 7.12a was an extrapolation of Peter and Weinert's data. Unfortunately, Kuo did not

give a detailed account of the development of Equation 7.12a. It is probable that the pre-exponential factor in Equation 7.12a was adjusted so that the correlation could be used to predict diffusion coefficients which led to the calculation of mass transfer coefficients which agreed with experimental mass transfer coefficients.

The most commonly used correlation for predicting Fischer-Tropsch mass transfer coefficients for gases in Fischer-Tropsch wax is the correlation of Calderbank and Moo-Young (1961). For small gas bubbles less than 2.5 mm in diameter, the mass transfer coefficient in the liquid phase was given by Calderbank and Moo-Young as;

$$k_L = c \cdot \left[ (D_{12})^2 \frac{\rho}{\mu} \right]^{1/3} \quad (7.13)$$

where  $D_{12}$  is the diffusion coefficient of the gas in the liquid,  $\rho$  and  $\nu$  are the density and viscosity of the liquid, and the constant  $c$  depends on the units of the other parameters. The correlation predicts that  $k_L$  is proportional to  $(D_{12})^{2/3}$ . If  $k_L$  values were calculated using the experimental diffusion coefficients from this study, the  $k_L$  values would be 2.5 to 3 times larger than the mass transfer coefficients calculated when either Equation 7.12a, b or c was used to estimate  $D_{12}$  and more than 3 times larger than the  $k_L$  values calculated when Equation 7.11 was used to estimate  $D_{12}$ .

Kuo (1983) and Satterfield and Huff (1980) have assumed that since their predicted values for  $D_{12}$  can be used in the Calderbank and Moo-Young correlation to accurately predict mass transfer coefficients, then their estimates of  $D_{12}$  must be reasonable. This argument is only valid if the Calderbank and Moo-Young correlation is correct. The argument is flawed by the fact that the Calderbank and Moo-Young correlation was based on low temperature (less than 50°C) experimental mass transfer data. For this reason, using consistently erroneous values of  $D_{12}$

in the Calderbank and Moo-Young correlation can lead to reasonable predictions of  $k_L$ , the mass transfer coefficient. If accurate values of  $D_{12}$  at the elevated temperatures typical of most industrial processes were used in the Calderbank and Moo-Young correlation, it would undoubtedly yield poor estimates of experimental mass transfer coefficients. These results indicate that new correlations for mass transfer coefficients at elevated temperatures are desperately needed.