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## Pressure and Temperature Dependence of the Diffusion of Methane in Helium

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Values of the binary molecular diffusion coefficient,  $D_{12}$ , for  $\text{CH}_4$  in He are obtained at atmospheric pressure and temperatures from 283 to 343 K and also at pressures from 47 to 112 atm at 303 K, with an uncertainty of 0.2%. Within this experimental uncertainty,  $D_{12}$  was linear with gas density. It fitted the equations  $\log D_{12} = -4.3256 + 1.6783 \log T$  and also the Lennard-Jones 12-6 formula using the fitted values  $\epsilon_{12}/k = 40.8 \text{ K}$  and  $\sigma_{12} = 3.186 \text{ \AA}$ .

### Experimental Section

The basic gas chromatographic system has been previously described (1). However, in the pressure-dependence studies, Nupro precision valves (Nupro Co., Cleveland, Ohio) both at the inlet and the outlet of the column were replaced by a pressure regulator (Consolidated Controls, Calif.) and a specially designed high-pressure control valve developed in Dr. J. C. Giddings' Laboratories, University of Utah, respectively.

The continuous elution gas chromatographic method employed here follows the same general procedure as in our previous report (1).

Helium gas (99.995% purity; Matheson Gas Products) was used as carrier gas. Flow rates were in the range 1.56–1.73 cm/s for the temperature-dependence studies and in the range of 0.95–1.02 cm/s for pressure-dependence studies. The methane was Matheson C.P. grade with a minimum purity of 99.0%. Since the accuracy of our measurements was better than 1%, this is a lower purity than desirable but fortunately the most likely impurity is hydrogen which is invisible to the flame ionization detector used and so has no effect on the result. If there were 1.0% of ethane present, our results would be 1/4% low which is about the limit of our experimental reliability. Hence the 99.0% purity of the methane is adequate.

Trace amounts of methane gas were injected directly into the column by a specially designed sampling valve (1). The sample chamber had been pressurized up to the same pressure as that of the column before the injection of sample occurred.

A 316 stainless steel column with a measured (1) effective length of 461.98 cm and a radius of 0.110 cm was employed.

In the temperature-dependence studies pressure at the inlet of the column was controlled at  $1.743 \pm 0.0015 \text{ atm}$  and the

temperature was in the range of  $(10-60) \pm 0.02 \text{ }^\circ\text{C}$ . The pressure gradient across the column was 0.002 atm, measured by using a 1.0-psi differential pressure transducer (Model KP 15, Whittaker Corp., North Hollywood, Calif.). Column pressure was measured by a mercury barometer at the outlet of the column.

In pressure dependence studies, the pressure was set between 700 and 1640 psi and the temperature was set at  $30 \pm 0.02 \text{ }^\circ\text{C}$ . Column pressure was measured by both an absolute pressure transducer (Model P2A, Whittaker Corp., Calif.) and a pressure gage (range 0–4000 psi; American Instrument Co., Inc., Silver Spring, Md.).

Sample eluted from the column was detected by a flame ionization detector. The current source from the FID was converted to voltage and amplified to about 1 V and then collected directly through a computer interfacing system to the disk memory system of the CDC computer at Oregon State University.

Four or more separate runs were conducted for each experimental condition. About 1000 data points were collected for each elution peak. The area, moments, skewness, kurtosis, velocity, and dispersion coefficient were determined numerically. The data points were then assembled into about 200 points by using a sequential 7 to 11 data points average routine. These were fitted to the theoretical equation (eq 1), where  $C$  is the

$$C = \frac{C_0 L}{2 \left[ \pi \left( \frac{D_{12}}{p} + \frac{r^2 v^2 p}{48 D_{12}} \right) \right]^{1/2} t^{3/2}} \exp \left\{ - \frac{(L - Vt)^2}{4t \left( \frac{D_{12}}{p} + \frac{r^2 v^2 p}{48 D_{12}} \right)} \right\} \quad (1)$$

instantaneous concentration at the exit of the column at time  $t$ ,  $C_0$  is the initial concentration at the inlet of the column,  $L$  is the column length,  $r$  is the column radius,  $v$  is the average linear flow velocity,  $t$  is the elution time, and  $p$  is the column pressure in atm.

### Results and Discussion

**Temperature Dependence.** Table I gives the average value of the diffusion coefficients of the helium-methane gas pair obtained at 10, 15, 20, 25, 30, 40, 50, 55, and 60  $^\circ\text{C}$ . The

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Table I. Average Values for Binary Molecular Diffusion Coefficients (He-CH<sub>4</sub>)

temp, °C	$\bar{D}_{12}$ , cm <sup>2</sup> /s (exptl)	$D_{12}$ , cm <sup>2</sup> /s (from eq 2)	difference (calcd - exptl)	$D_{12}$ , cm <sup>2</sup> /s (from eq 3)	difference (calcd - exptl)
10 ± 0.02	0.6160 ± 0.0014 <sup>a</sup>	0.6160	0.0000	0.6160	0.0000
15 ± 0.02	0.6316 ± 0.0009	0.6344	0.0028	0.6344	0.0028
20 ± 0.02	0.6489 ± 0.0009	0.6530	0.0041	0.6529	0.0040
25 ± 0.02	0.6736 ± 0.0022	0.6718	-0.0018	0.6717	-0.0019
30 ± 0.02	0.6929 ± 0.0018	0.6908	-0.0021	0.6900	-0.0029
40 ± 0.02	0.7285 ± 0.0017	0.7295	0.0010	0.7291	0.0006
50 ± 0.02	0.7682 ± 0.0022	0.7690	0.0008	0.7689	0.0007
55 ± 0.02	0.7895 ± 0.0033	0.7891	-0.0004	0.7890	-0.0005
60 ± 0.02	0.8078 ± 0.0034	0.8094	0.0016	0.8093	0.0015

<sup>a</sup> Uncertainties are obtained from the least-squares fit of the instrument output data for the chromatographic peak to eq 1.

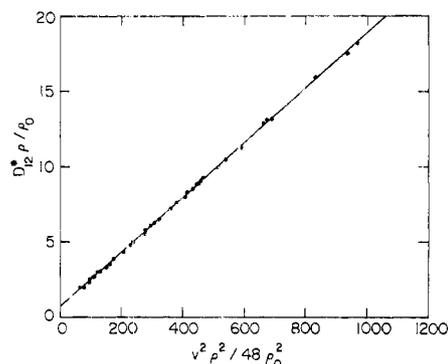


Figure 1.  $-\log D_{12}$  vs.  $\log T$  for the He-CH<sub>4</sub> system. The solid line is the least-squares best fit.

precision of the measurements was in the range of 0.14–0.42%. The value of 0.6736 at 30 °C is in excellent agreement with the value 0.6735 produced later by the superior stopped-flow technique and reported in ref 1. Further indication of the precision and reliability of the measurements is shown by the least-squares plot of  $\log D_{12}$  vs.  $\log T$  in Figure 1. The correlation coefficient is 0.9986. The slope of this least-squares straight line gave a  $1.6783 \pm 0.0192$  temperature power dependence of  $D_{12}$  with 90% confidence (from the relationship  $D_{12} = AT^m$ ). This value agrees well with the literature values, 1.6–1.8 (2). It is lower than Marrero and Mason's recommended value (3) of 1.750 but in view of the scatter of the data they used, their value is inevitably imprecise. Accordingly, we offer the equation

$$\log D_{12} = -4.3256 + 1.6783 \log T \quad (2)$$

as the best currently available equation for predicting the diffusion coefficient of methane in helium. The intercept has a 90% confidence interval of  $\pm 0.0473$ . The uncertainties of the power and intercept are mutual since uncertainty in one produces uncertainties in the other. The predictive power of eq 2 is thus much greater than the uncertainties of the coefficients suggest, and the significant figures are necessary to reflect the precision of the data.

The data were also fitted to the theoretical equation quoted by Reid and Sherwood (4)

$$D_{12} = (1.858 \times 10^{-3}) T^{3/2} \{ (M_1 + M_2) / M_1 M_2 \}^{1/2} / P \sigma_{12}^2 \Omega_D \quad (3)$$

where  $M_1$  and  $M_2$  are the molecular weights of He and CH<sub>4</sub>,  $P$  is the pressure in atmospheres,  $\sigma_{12}$  is the collision diameter in angstroms, and  $\Omega_D$  is the collision integral, which is a function of the force constant  $\epsilon_{12}/k$ . The method of Youssef et al. (5) was used to fit diffusion data and obtain the values  $\epsilon_{12}/k = 40.8$  K and  $\sigma_{21} = 3.194$  Å. When these values were used with eq 3, interpolating in the table of collision integrals (6) for  $\Omega_D$ , a slight systematic deviation from the data was found and corrected by assuming  $\sigma_{12} = 3.186$  Å instead of 3.194 Å. The

Table II. Average Values for Binary Molecular Diffusion Coefficients (He-CH<sub>4</sub>)

$\bar{P}$ , atm	$\bar{D}_{12}$ , cm <sup>2</sup> /s
47.65	0.014 48 ± 0.000 08 <sup>a</sup>
56.16	0.012 31 ± 0.000 07
71.48	0.009 721 ± 0.000 04
82.37	0.008 386 ± 0.000 07
93.94	0.007 384 ± 0.000 05
95.30	0.007 240 ± 0.000 03
98.71	0.007 042 ± 0.000 07
100.75	0.006 858 ± 0.000 03
111.64	0.006 228 ± 0.000 04

<sup>a</sup> Uncertainties are obtained from the least-squares fit of the instrument output data for the chromatographic peak to eq 1.

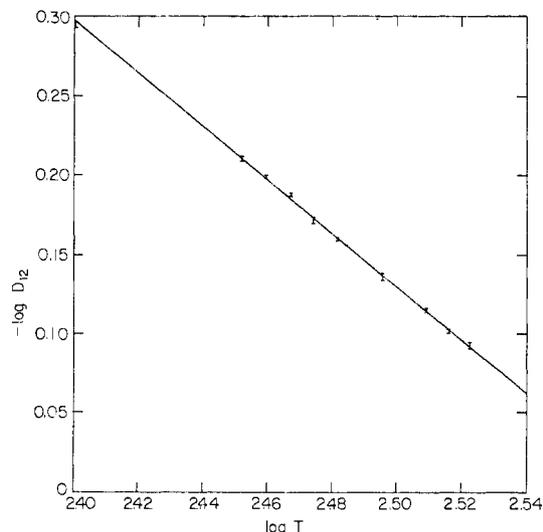


Figure 2. Least-squares of best fit for the plot of reduced dispersion coefficient  $D_{12}^* \rho / \rho_0$  (cm<sup>2</sup>/s) vs. reduced velocity  $v^2 \rho^3 / 48 \rho_0^2$  (cm<sup>2</sup>/s<sup>2</sup>) for the He-CH<sub>4</sub> system.

results are shown in Table I with the results from eq 2. Both equations appear to fit the data equally well.

**Pressure Dependence.** Table II shows the average binary diffusion coefficient,  $D_{12}^{(p)}$ , at  $30 \pm 0.02$  °C at various column pressures. The precision and accuracy of the measurements were tested by plotting  $D_{12}^* \rho / \rho_0$  vs.  $\rho^2 v^2 / 48 \rho_0^2$  (from the equation  $D_{12}^* \rho / \rho_0 = D_{12} + (r^2 / D_{12}) (\rho^2 v^2 / 48 \rho_0^2)$ , where  $\rho$  and  $\rho_0$  are the density of helium at the column pressure  $p$  and at atmospheric pressure, respectively;  $D_{12}^*$  is the observed dispersion coefficient, resulting from both diffusion and from the flow profile and  $D_{12}$  is the binary molecular diffusion coefficient at 30 °C and 1 atm pressure. The density,  $\rho$ , was calculated from

$$\rho = PM_1 / ZRT$$

where  $Z$  is the compressibility factor for helium gas and  $R$  is the gas constant. Figure 2 shows a least-squares best straight

line fit of the above experimental points. The correlation coefficient is 0.9994. This confirms that the He-CH<sub>4</sub> system behaves ideally, that is that  $D_{12}$  is linear with gas density within at most 0.2% up to at least 112 atm (116 kg/cm<sup>2</sup>) and that the Taylor equation for the overall dispersion  $D_{12}^*$  is precisely followed. The intercept gave a value of the diffusion coefficient at atmospheric pressure of 0.6857 cm<sup>2</sup>/s. This value agrees moderately with our previous measured value, 0.6929, and the values 0.6895 cm<sup>2</sup>/s calculated from Marrero and Mason's (3) best fit equation. The slight discrepancy of this pressure-extrapolated value from the other values is attributed to uncertainty in the ancient pressure gage used for these high pressures.

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## Equilibrium Solubilities of Methane, Carbon Monoxide, and Hydrogen in Water and Sea Water

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Measured Bunsen solubility coefficients reported in the literature are used to derive functions that permit accurate calculation of the concentration of methane, carbon monoxide, and hydrogen in water and sea water at equilibrium with the normal atmosphere. Bunsen coefficients are fitted to equations established by Weiss which give Bunsen coefficients as functions of temperature and salinity. Tables of Bunsen coefficients covering the temperature range -2 to +30 °C and the salinity range 0-40 parts per thousand are calculated for each gas from the fitted equations. The data are also fitted to an atmospheric equilibrium solubility function, which has a form similar to the Bunsen coefficient equation, but which includes the atmospheric gas concentration as a variable. Coefficients for this equation are given to allow calculation of the concentration of dissolved methane, carbon monoxide, and hydrogen in equilibrium with moist air at 1 atm total pressure in units of nL/L, nmol/L, nL/kg, and nmol/kg sea water.

Since Craig and Gordon (7) reported finding nitrous oxide in sea water, the list of chemically unstable gases found in the ocean has grown to include methane (25), carbon monoxide (28), hydrogen (36), and others (26). These unstable gases are produced biogenically and there has been considerable study of factors governing their release, consumption, and distribution in sea water. Seiler and Schmidt (24) have reviewed the early studies of these gases in the ocean and the work continues today at an intensified pace (5, 6, 14, 23). Oceanic surface waters appear to act as a source to the atmosphere for most reduced gases (14, 23, 27, 41) with bottom water, oxygen minimum zones, and anoxic waters perhaps acting as sinks (4, 5, 6, 17). In the search for sources and sinks of gases which are biologically produced or consumed, we must know the normal atmospheric equilibrium solubility values for these gases in sea water as a function of temperature and salinity.

Bunsen coefficients for methane, carbon monoxide, and hydrogen are found in the literature (8, 10, 13, 37, 40), but equations expressing atmospheric solubilities as functions of temperature and salinity have not been determined for these reduced gases, as they have for oxygen, nitrogen, argon and various inert gases (31, 32, 34). Since previous studies of reduced gases have not derived equations for atmospheric equilibrium solubilities, we calculate here the numerical ex-

pressions that permit rapid, accurate determination of atmospheric solubilities of methane, carbon monoxide, and hydrogen. Our derivations are based on the equations of Weiss (31), which express atmospheric equilibrium solubility as a function of temperature and salinity. Nitrous oxide is not considered here, since there have been no measurements of nitrous oxide solubilities over temperature and salinity ranges large enough to allow application of our method.

#### Data Analysis

**Raw Data.** Precise measurements of Bunsen solubility coefficients,  $\beta$ , are available in the literature for methane (40), carbon monoxide (10, 37), and hydrogen (8, 13) in distilled water and sea water over various temperature and salinity ranges. The Bunsen coefficient,  $\beta$ , is defined as the volume of gas, reduced to 0 °C and 1 atm of pressure (standard temperature and pressure) contained in a unit volume of water at the temperature of the measurement when the partial pressure of the gas is 1 atm. Only raw, unsmoothed solubility data for methane, carbon monoxide, and hydrogen, given by the various authors, were used in our analysis. Selection of data was based upon the temperature and salinity ranges of measurements, level of agreement with other workers for distilled water solubilities, and the precision and susceptibility of the experimental method to systematic errors. Most of the data used (8, 10, 40) were determined by using microgasometric techniques (9). Douglas (9) estimated the accuracy of microgasometric methods to be about  $\pm 0.26\%$ . Discussions of accuracies of other methods are given by the individual authors and will receive only limited mention here.

We have chosen the Bunsen solubility data of Yamamoto et al. (40) as the best data for methane since it covers a wide range of temperatures and salinities and compares well with some earlier data for distilled water (2, 3). The raw solubility data of Douglas (10) was used for carbon monoxide. Douglas' values of chlorinity were converted to salinity, by using the equation  $S_{\text{‰}} = 1.80655(\text{Cl}_{\text{‰}})$  (39). The lowest salinity at which Douglas measured solubility was 27.8 ‰; we therefore have combined his data with the distilled water measurements made by Winkler (37) for our calculations. The oxygen solubility measurements made by Winkler (37) as part of the same work during which he measured carbon monoxide solubility, differ by less than 0.4% from the oxygen data reported by Weiss (31). This leads us to believe that Winkler's 1906 measurements were