

# Diffusivity Measurements in Some Organic Solvents by a Gas-Liquid Diaphragm Cell

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A diaphragm cell has been developed for the measurement of diffusion coefficients of gases in liquids. The diaphragm cell is operated batchwise with respect to both gas and liquid phases, and the diffusion process is followed by means of the gas pressure decrease which is recorded by means of a pressure transducer. The diaphragm cell has been calibrated with some well-known gas-liquid systems. The present diaphragm cell was shown to be very suitable for the determination of diffusion coefficients at higher temperatures. The diffusion coefficient of CO<sub>2</sub> and propene in toluene has been measured at temperatures ranging from 298 to 328 K. The diffusivity for various other gas-liquid systems has been determined at 298 K.

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## 1. Introduction

The molecular diffusivity is an important transport property and is usually needed in the interpretation of gas absorption experiments into liquids. In the deduction of chemical reaction kinetics from reaction-enhanced gas absorption experiments, knowledge of the diffusivity is indispensable (1). Also in the design of gas-liquid reactors, transport properties like the molecular diffusivity are necessary. Recently Wong and Hayduk (2) reviewed diffusivity data and diffusivity correlations available in open literature.

Accurate diffusion measurements in model reactors like the laminar jet, wetted sphere, or laminar film reactors are hard to obtain, especially at higher temperatures. Moreover, rather large amounts of chemicals are needed, and unexpected additional turbulence phenomena may occur. The major drawbacks of these experimental methods seem to be overcome by methods like the gas-liquid diaphragm cell and the Taylor-dispersion method: operation at higher temperatures is relatively easy, and relatively small amounts of chemicals are needed. A strict requirement for successful use of these latter methods is the absence of a reaction between gas and liquid, whereas a (very) slow gas-liquid reaction does not hamper the diffusivity measurements in laminar jet, wetted sphere, or laminar film reactors.

Pioneering work on the application of liquid-liquid diaphragm cells for diffusivity measurements was carried out by Stokes (3). The use of a gas-liquid diaphragm cell method for the measurement of gas diffusivities in liquids is more recent (4-6).

In the present work a modified diaphragm cell has been developed for diffusion measurements of gases in liquids: the pressure decrease in the gas compartment of the batchwise operated diaphragm cell was recorded by means of a pressure transducer. Diffusion measurements of gases into water and various organic liquids at temperatures ranging from 298 to 328 K have been carried out in this diaphragm cell.

## 2. Experimental Section

**2.1. Setup.** A schematic drawing of the gas-liquid diaphragm cell used in the present work is shown in Figure 1. The

diaphragm cell consists of two cylindrical all-glass compartments for the gas and liquid phases, respectively, which are divided by a stainless steel ring in which the diaphragm has been welded. Each glass compartment has an internal volume of about 375 mL and an internal diameter of about 70 mm. The top and bottom of the cell are formed by two identical stainless steel flanges on which the propeller-type stirrers are mounted. A horseshoe magnet, coated with Teflon, is attached to each stirrer and coupled magnetically with a variable-speed motor. The flanges, glass compartments, and diaphragm ring, divided by viton gaskets, are held tightly together by means of six drawbars. The diaphragm ring and flanges are made out of 316 stainless steel. The flanges and the glass compartments are equipped with a double wall through which thermostated water is led in order to keep the whole diaphragm cell at a constant temperature ( $\pm 0.1$  K). Each flange contains two and each glass compartment contains one fluid in- or outlet.

The diaphragm is a 2-mm-thick disk made out of sintered 316 stainless steel with a narrow pore size distribution and a mean pore diameter of about 10  $\mu\text{m}$ . The porosity of the diaphragm is about 50%. The diaphragms were obtained from Pressmetal Krebsöge (SIKA R 10). The diaphragm material was sufficiently wettable by the applied liquids, which is required in order to avoid captured air or gas in the diaphragm.

The diaphragm cell is operated batchwise with respect to both gas and liquid phases. The pressure decrease in the gas compartment is recorded as a function of time by means of a pressure transducer (range 0-1 bar; accuracy  $\pm 0.0005$  bar) which is connected to an Apple IIe computer. A flow scheme of the entire experimental setup is provided in Figure 2.

**2.2. Procedure.** The interpretation of diffusivity experiments in a diaphragm cell assumes that the whole diaphragm is filled with liquid. Therefore, in the experimental procedure extreme care must be taken to avoid the presence of captured air or gas in the diaphragm.

At the start of an experiment the diaphragm cell is filled with degassed liquid till the liquid level is somewhat above the diaphragm. This condition is maintained for several hours in order to allow the diaphragm to become filled entirely with liquid. The amount of time needed for this depends on the ease of wettability of the diaphragm by the liquid and was found to range from 3 h for toluene to 20 h for water. After this, the surplus of liquid is sucked from the diaphragm till the surface of the diaphragm has a gleaming appearance. This gleaming appearance is a measure that the diaphragm is just filled with liquid, and this appearance should be maintained throughout the diffusion experiment. Subsequently, the gas compartment is filled with pure gas which has been led through a thermostated gas saturator, and the diffusion experiment is started. The diffusion experiment takes typically 12-48 h to obtain a reliable diffusion coefficient. Obviously, allowing equilibrium to be reached in order to determine simultaneously the gas solubility takes much longer.

**2.3. Theory.** Assuming vapor-liquid equilibrium at the gas-liquid interface and ideal mixing conditions in both compartments, the following mass balances for the gas and liquid phases describe the physical absorption process in a diaphragm cell

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$$V_g \frac{dC_g}{dt} = -k_L(mC_g - C_L)A \quad (1)$$

$$V_L \frac{dC_L}{dt} = k_L(mC_g - C_L)A \quad (2)$$

with initial conditions

$$t = 0 \quad C_g(t=0) = C_g^0 \quad (3)$$

$$t = 0 \quad C_L(t=0) = C_L^0 \quad (4)$$

and with the solubility  $m$  defined as the ratio of liquid-phase and gas-phase concentrations of the solute gas at equilibrium conditions

$$m = (C_L/C_g)_{\text{equil}} \quad (5)$$

Solving eqs 1–4, under the assumption that  $C_L^0 = 0$ , yields for the gas-phase concentration the following expression:

$$C_g = \frac{C_g^0}{V_g + mV_L} \left\{ V_g + mV_L \exp \left[ -k_L \left( \frac{1}{V_L} + \frac{m}{V_g} \right) At \right] \right\} \quad (6)$$

Interpretation of the experimental data according to expression 6 yields a value for  $k_L A$ . Since the assumptions underlying the film theory are exactly fulfilled in the case of a diaphragm cell, this  $k_L A$  value is proportional to the diffusion coefficient:

$$k_L A = \frac{D_{\text{eff}} A}{\delta} = D \frac{A \gamma}{\delta} = Df \quad (7)$$

The proportionality factor  $f$  is only dependent on diaphragm properties and can be obtained easily via a gas–liquid system with a known diffusion coefficient. The measured  $k_L A$  value should be independent of the stirring rates in the gas and liquid compartments as it is assumed in the interpretation that no mass transfer resistances exist outside the diaphragm.

**2.4. Characterization and Calibration.** In order to show the suitability of the present diaphragm cell for diffusivity measurements, a number of experiments have been carried out with systems for which the diffusivities are well-known and have been confirmed by various methods (6, 7). These measurements were also used to calibrate the diaphragm and to obtain the value for the proportionality factor  $f$  (see eq 7). The characterization experiments are summarized in Table I.

In the interpretation of the diffusivity experiments, it is assumed that no mass transfer resistances exist outside the diaphragm. In order to validate this assumption the stirring rate in the liquid-containing compartment has been varied. No influence of this stirring rate on the calculated proportionality factor was observed within experimental accuracy. Also the stirring rate in the gas compartment did not affect this factor. The characterization experiments reported in Table I show that the value of the proportionality factor was not dependent on the gas–liquid system. The effect of temperature on the value for this factor was also negligible within experimental accuracy.

From the calibration experiments a mean value of 0.40 was obtained for the proportionality factor of the diaphragm used in the diffusivity experiments. From this value a porosity/tortuosity factor can be calculated of about 0.27, which seems a very reasonable value for a diaphragm with 50% porosity. The accuracy of the determined proportionality factor is estimated to be about 6%.

Summarizing, the diffusivity experiments with some well-known systems showed the validity of the present diaphragm cell, in which the diffusion process is followed by means of the gas pressure decrease, for the measurement of diffusion coefficients of gases into liquids.

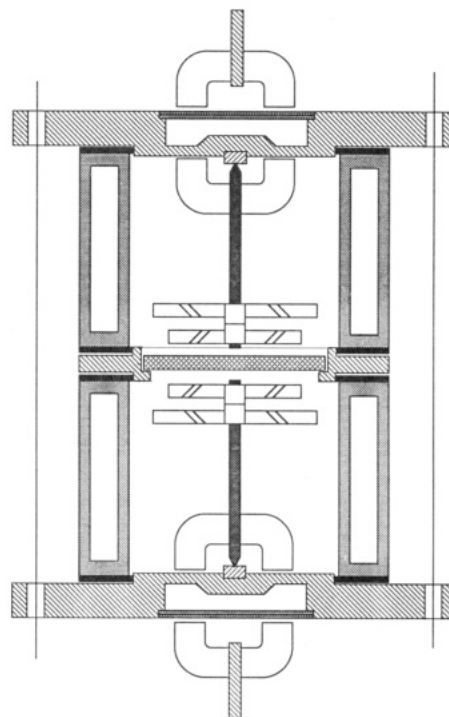


Figure 1. Gas–liquid diaphragm cell.

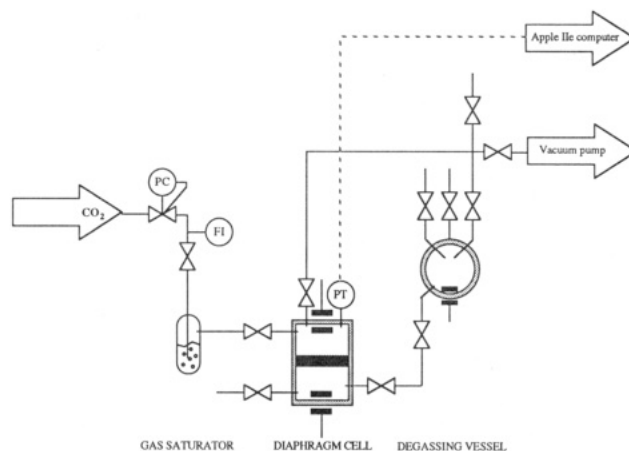


Figure 2. Experimental setup.

Table I. Diaphragm Calibration Experiments

solvent	gas	T/K	$m$	$D/(10^{-9} \text{ m}^2 \text{ s}^{-1})$	ref	$N_L/\text{rpm}$	$f/m$
water	CO <sub>2</sub>	298	0.82	1.92	7	66	0.391
water	CO <sub>2</sub>	298	0.82	1.92	7	60	0.405
water	CO <sub>2</sub>	328	0.50	3.68	7	40	0.384
ethanol	CO <sub>2</sub>	298	2.65	3.86	6	78	0.408
water	N <sub>2</sub> O	298	0.61	1.79	7	80	0.375
1 M MDEA in water	N <sub>2</sub> O	298	0.58	1.26	7	98	0.431

### 3. Results

**3.1. Toluene.** The diffusivity of CO<sub>2</sub> and propene into toluene has been studied as a function of temperature by means of the diaphragm cell technique. The experimentally obtained diffusion coefficients at 298, 308, 318, and 328 K are presented in Tables II and III and Figures 3 and 4 for CO<sub>2</sub> and propene, respectively. Some data are available in open literature for the diffusivity of CO<sub>2</sub> in toluene (5, 8–10). These literature values which were obtained by various experimental techniques are in reasonable agreement with the presently obtained diffusion coefficients of CO<sub>2</sub> in toluene as is shown in Table II and Figure 3. Diffusivities of propene in toluene seem not to have been

Table II. Diffusion Coefficients of CO<sub>2</sub> in Toluene

T/K	m	D/(10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup> )	method	ref
293		3.44	horizontal film	10
298		4.33	laminar jet	8
298		4.6	capillary cell	9
298		4.61	G-L diaphragm cell <sup>a</sup>	5
298	2.35	4.14	G-L diaphragm cell	present work
298	2.35	3.91	G-L diaphragm cell	present work
308	2.14	4.35	G-L diaphragm cell	present work
308	2.14	4.48	G-L diaphragm cell	present work
318	1.94	5.01	G-L diaphragm cell	present work
318	1.94	4.94	G-L diaphragm cell	present work
323		6.69	capillary cell	9
328	1.77	5.60	G-L diaphragm cell	present work
328	1.77	5.54	G-L diaphragm cell	present work

<sup>a</sup> Gas-liquid diaphragm cell.

Table III. Diffusion Coefficients of Propene in Toluene Obtained in the Present Study with the Gas-Liquid Diaphragm Cell

T/K	m	D/(10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup> )	T/K	m	D/(10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup> )
298	15.5	2.20	318	9.55	3.85
298		2.43	318		4.21
298		2.18	328	7.06	5.07
308	12.7	2.97	328		5.07
308		2.89	328		5.11
308		2.93			

reported in open literature. Notwithstanding the high gas solubility of propene in toluene, good reproducibility of the diffusivity measurements for this system could be obtained by applying quite low initial propene pressures (typically 0.2 bar).

The influence of temperature on the observed diffusion coefficients could be described by an Arrhenius relationship:

$$D_{\text{CO}_2}/(\text{m}^2 \text{s}^{-1}) = 1.46 \times 10^{-7} \exp\left(\frac{-1073}{T/\text{K}}\right) \quad (8)$$

$$D_{\text{prop}}/(\text{m}^2 \text{s}^{-1}) = 1.75 \times 10^{-5} \exp\left(\frac{-2671}{T/\text{K}}\right) \quad (9)$$

**3.2. Various Systems.** The diffusion coefficients for various, rather arbitrarily chosen, gas-liquid systems have been measured by means of the diaphragm cell technique. Although the gas-liquid systems investigated varied widely in gas solubility and diffusivity, the present diaphragm cell was found to produce reliable diffusivity data. The observed diffusivities and available literature values are summarized in Table IV. For propene in water the present diffusion coefficients appear to be in ac-

Table IV. Diffusion Coefficients in Various Solvents

system	T/K	m	D/(10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup> )	method	ref
propene/water	298	0.15	0.68	laminar jet	11
propene/water	298	0.15	1.08	G-L diaphragm cell <sup>a</sup>	present work
propene/water	298	0.15	1.24	G-L diaphragm cell	present work
propene/water	298	0.16	1.10	laminar jet	13
propene/water	298		1.44	L-L diaphragm cell <sup>b</sup>	14
N <sub>2</sub> O/toluene	298	3.41	3.76	G-L diaphragm cell	present work
N <sub>2</sub> O/toluene	298	3.41	3.82	G-L diaphragm cell	present work
N <sub>2</sub> /toluene	298	0.12	6.19	G-L diaphragm cell	present work
N <sub>2</sub> /toluene	298	0.12	6.07	G-L diaphragm cell	present work
CO <sub>2</sub> /chlorobenzene	298	2.32	3.69	G-L diaphragm cell	present work
CO <sub>2</sub> /chlorobenzene	298	2.32	3.93	G-L diaphragm cell	present work
H <sub>2</sub> /cyclohexane	298		7.08	not reported	15
H <sub>2</sub> /cyclohexane	298	0.11	9.63	G-L diaphragm cell	present work
H <sub>2</sub> /cyclohexane	298	0.11	9.11	G-L diaphragm cell	present work
H <sub>2</sub> /cyclohexane	298	0.11	9.21	G-L diaphragm cell	present work
H <sub>2</sub> /cyclohexane	298		17.3	dissolving bubble	12

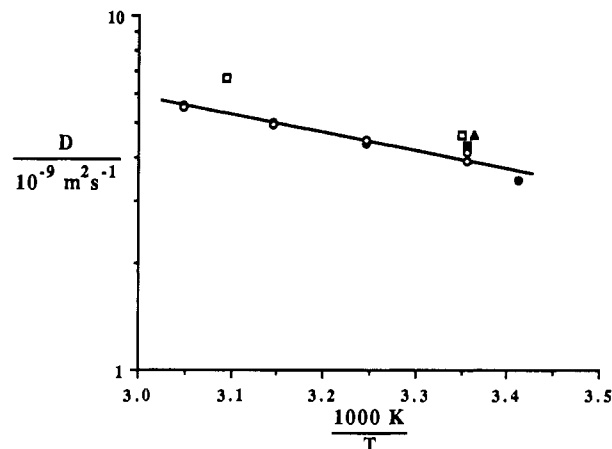
<sup>a</sup> Gas-liquid diaphragm cell. <sup>b</sup> Liquid-liquid diaphragm cell.

Figure 3. Experimental data for the CO<sub>2</sub> diffusivity in toluene (log  $D$  vs  $1000/T$ ): O, present work; ●, Sovova and Prochazka (1976); ■, Tang and Himmelblau (1965); □, McManamey and Woolen (1973); △, Takeuchi et al. (1975).

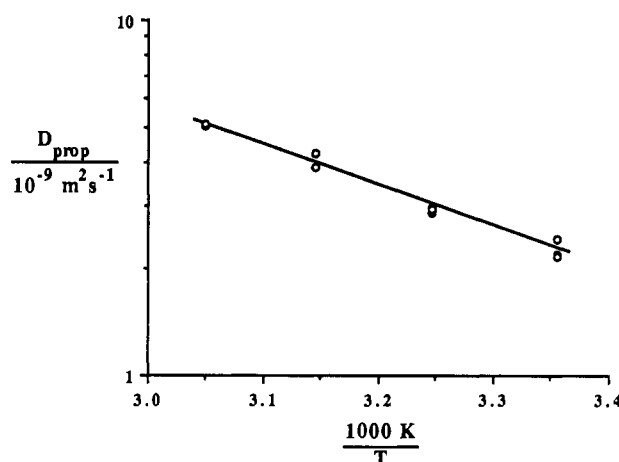


Figure 4. Experimental data for the propene diffusivity in toluene (log  $D$  vs  $1000/T$ ).

ceptable agreement with literature data; the data presented by Unver and Himmelblau (11) are somewhat low. In judging the diffusivity data for H<sub>2</sub> in cyclohexane, it should be noted that the dissolving bubble method applied by Sporka et al. (12) is likely to yield too high diffusivities because the assumption of a stagnant liquid surrounding the gas bubble is easily violated in the case of rapidly diffusing gases.

The diaphragm cell in its present configuration appears to be suitable for diffusivity measurements for gas-liquid systems which show a wide variation in gas solubilities and diffusion

coefficients. A decrease of the ratio of the volumes of the gas compartment with respect to the liquid compartment would increase the suitability of the present cell for systems with very low gas solubilities, as in the present configuration the accuracy of the pressure transducer tends to become limiting in the case of low absolute pressure decreases. For systems with high gas solubilities in combination with high diffusivities, a thicker diaphragm offers the possibility to determine more exactly the initial conditions and therefore facilitates experimentation.

#### 4. Conclusions

A modified diaphragm cell has been developed for the measurement of diffusion coefficients of gases in liquids. The diaphragm cell is operated batchwise with respect to both gas and liquid phases, and the absorption process is followed by means of the gas pressure decrease which is recorded by a pressure transducer.

The present diaphragm cell was shown to be very suitable for the determination of diffusion coefficients at higher temperatures.

The diffusion coefficients of CO<sub>2</sub> and propene in toluene have been measured at temperatures ranging from 298 to 328 K. The diffusivity for various other gas-liquid systems has been determined at 298 K.

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#### Glossary

<i>A</i>	diaphragm surface area
<i>C</i>	concentration
<i>D</i>	diffusion coefficient
<i>f</i>	proportionality factor (eq 6)
<i>k</i>	mass transfer coefficient
<i>m</i>	dimensionless solubility

<i>t</i>	time
<i>T</i>	temperature
<i>V</i>	volume

#### Greek Letters

$\delta$	diaphragm thickness
$\epsilon$	porosity
$\gamma$	porosity/tortuosity factor ( $\gamma = \epsilon/\tau$ )
$\tau$	tortuosity

#### Subscripts / Superscripts

eff	effective
g	gas phase
L	liquid phase

**Registry No.** CO<sub>2</sub>, 124-38-9; N<sub>2</sub>O, 10024-97-2; N<sub>2</sub>, 7727-37-9; propene, 115-07-1; toluene, 108-88-3; chlorobenzene, 108-90-7.

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## Surface Tension Measurements of Glycerol with Organic Cosolvents

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Surface tension data of binary mixtures of glycerol with methanol, 1-propanol, acetic acid, propionic acid, dimethyl sulfoxide, and *N,N*-dimethylformamide have been measured with a Du Nöuy torsion balance by a ring-detachment method. The values of the excess surface tension for these mixtures were also calculated.

### 1. Introduction

The literature dealing with the surface tension of binary mixtures is extensive (1-3). Such systems involving alcohols are interesting because of their inherent nature of forming associations in the form of hydrogen bonds within themselves or

with other components. This property is directly reflected in various physical parameters, such as densities (4), viscosities (5), and surface tensions (6).

The aim of this paper is to determine the surface tension values of binary mixtures of glycerol with organic cosolvents, e.g. methanol, 1-propanol, acetic acid, propionic acid, dimethyl sulfoxide, and *N,N*-dimethylformamide. The values of the excess surface tension for these binary mixtures have also been computed.

### 2. Experimental Section

The chemicals used in this work were methanol (99.8%), 1-propanol (99.5%), acetic acid (99.8%), *N,N*-dimethylformamide (99.5%), and dimethyl sulfoxide (99.5%), which were supplied by E. Merck, and propionic acid (99%) and glycerol (99.5%) were supplied by BDH. Methanol and 1-propanol were

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