

## *Measurement of saturated solubilities and diffusion coefficients of pure gases to mineral oil*

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The present paper deals with measurements of the diffusion coefficients as well as the saturated solubilities of single component gases such as N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> to a mineral oil. The method to determine the diffusivity is based upon measuring the pressure changes caused by the one-dimensional diffusion between the gas and the oil enclosed in an airtight container. For N<sub>2</sub> and O<sub>2</sub> the profiles of the measured pressure changes agree well with those predicted by diffusion theory, whereas that is not the case with CO<sub>2</sub>. Although the reason why CO<sub>2</sub> does not seem to obey diffusion theory has yet to be studied, it may suggest the possibility that the diffusion coefficient varies with the pressure, considering that the range of pressure change in the diffusivity measurement was much larger for CO<sub>2</sub> than for the other two gases. The diffusion coefficient values of N<sub>2</sub> and O<sub>2</sub> obtained by this method fell within  $\pm 30\%$  around the average. Moreover the solubility measurements have made clear that Henry's law holds true between the three pure gases and the oils tested, and that O<sub>2</sub> and CO<sub>2</sub> dissolve into the oil approximately two and ten times more, respectively, than N<sub>2</sub>.

### NOTATION

$A$	cross sectional area of container	$m^2$	$T$	temperature	K
$a, b$	van der Waals constants		$p_i$	initial pressure	Pa
$c(y, t)$	molar gas concentration in oil	$mol/m^3$	$y$	depthwise distance from oil surface	m
$C(y, s)$	Laplace transform of $c(y, t)$		$R$	gas constant	$Pa \cdot m^3 / (mol \cdot K)$
$c_i$	initial molar gas concentration	$mol/m^3$	$s$	Laplace operator	
$c_s$	saturated molar concentration	$mol/m^3$	$t$	time	s
$l$	depth of oil	m	$V$	gas volume	$m^3$
$n$	mole number of gas	mol	$\alpha$	reciprocal Henry's constant	$mol / (m^3 \cdot Pa)$
$p(t)$	gas pressure	Pa	$\gamma$	molar ratio between N <sub>2</sub> and O <sub>2</sub>	
$P(s)$	Laplace transform of $p(t)$		$\kappa$	diffusion coefficient of gas to oil	$m^2/s$
			$\lambda$	radius of gas bubble	mm

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## 1. INTRODUCTION

In liquid systems which transmit energy and signals, bubbles in the liquid can sometimes seriously damage the system's performance, and therefore have long been an important subject of study in engineering. When the liquid is a mineral oil, which contains gas at about 10 % in volumetric ratio but in contrast has a very low vapor pressure of several Pa, diffusion of a gas into the oil becomes a major concern, whereas the role of vapor is usually negligible.

Growth and shrinkage of bubbles in a liquid subject to diffusion have been studied by Epstein and Plesset<sup>(1)</sup> and many others<sup>(2-8)</sup>. Of these, the works dealing with bubbles in an oil<sup>(4-8)</sup> include an attempt to identify the essential physical quantity dominating the phenomenon, that is, the diffusion coefficient of the gas to the oil. The method adopted there was observing diameter changes of a minute spherical bubble rested in the oil and fitting the data to their theoretical predictions, while "air" was always used as the gas in the bubble. Since air is mainly composed of nitrogen and oxygen, however, the question naturally occurs if a mixed gas really has an inherent diffusivity to be identified.

In place of the traditional "bubble" method, the present paper offers a new method to find the diffusion coefficient of a gas to an oil. The new method utilizes the pressure change of the gas having a constant volume and temperature and diffusing one-dimensionally into the oil. Three different kinds of single component gases such as nitrogen, oxygen and carbon dioxide and VG10 mineral oils are employed for test. The saturated molar concentrations of the three gases to the oils are measured ahead of the diffusivity measurement. Also discussed is whether a mixed gas can be regarded as 'pure' in the bubble diffusion problem.

## 2. PRINCIPLE OF DIFFUSION COEFFICIENT MEASUREMENT

Since diffusion coefficient is not a physical quantity that can be directly measured, the following procedure is necessary to empirically identify its value; paying attention to another physical quantity in some diffusion process and comparing its variation with what diffusion theory predicts. In order to make the measurement successful, the experimentally constructed diffusion process needs to accord with the theoretically supposed one as closely as possible and the selected physical quantity should be one which can be accurately measured. The traditional "bubble" method does not necessarily meet those requirements; in addition to the difficulties in accurately measuring diameters of minute bubbles, it is usually not easy to satisfactorily match the experimental model with the theoretical. In addition, the uncertainty of the surface tension value can work to undermine the reliability of the measurement when the bubble becomes small.

In the present paper attention is turned to the diffusion between a gas and an oil confined in a cylindrical vessel having a uniform cross section (Fig.1). It is expected that this process makes a better method to measure diffusion coefficients, considering that the surface tension has little influence on the process and the discrepancy between the theoretical model

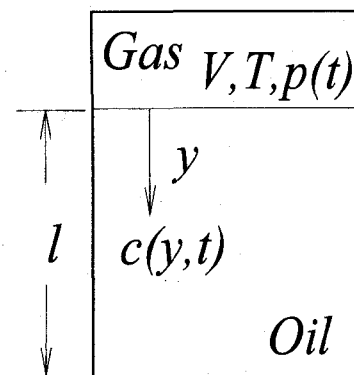


Fig.1 One-dimensional gas-oil diffusion model

and the experimental setup can be smaller than that in the traditional method. The following assumptions are introduced to build a mathematical model:

- (i) Diffusion occurs normal to the gas-oil interface and is governed by a one-dimensional diffusion equation.
- (ii) Diffusion coefficient is independent of the pressure.
- (iii) The gas and the oil have the same constant temperature.
- (iv) The relation between the saturated gas concentration in the oil and the pressure obeys Henry's law.
- (v) At any instant the oil surface is saturated with the gas at its pressure.
- (vi) At the initial instant the gas is uniformly dissolved in the oil up to the saturation point.
- (vii) The oil vapor pressure is negligible in the total gas pressure.

According to Assumption (i) the molar gas concentration at any location in the oil is determined by the one-dimensional diffusion equation

$$\frac{\partial c}{\partial t} = \kappa \frac{\partial^2 c}{\partial y^2} \quad (1)$$

The initial and boundary conditions to solve Eq.(1) are given as follows:

initial condition

$$c(y, -0) = c_i = \alpha p_i \quad (2)$$

boundary conditions

$$c(0, t) = c_s = \alpha p(t) \quad (3)$$

$$\left( \frac{\partial c}{\partial y} \right)_{y=l} = 0 \quad (4)$$

Taking the Laplace transform of Eq.(1) with the initial condition (2) yields

$$\kappa \frac{\partial^2 C}{\partial y^2} = sC - \alpha p_i \quad (5)$$

Solving the ordinary differential equation (5) and applying the boundary conditions (3) and (4) to the solution gives the gas concentration in the Laplace domain.

$$C(y, s) = \frac{c_i}{s} + \alpha \left\{ P(s) - \frac{p_i}{s} \right\} \left\{ \cosh \left( y \sqrt{\frac{s}{\kappa}} \right) - \sinh \left( y \sqrt{\frac{s}{\kappa}} \right) \tanh \left( l \sqrt{\frac{s}{\kappa}} \right) \right\} \quad (6)$$

The molar flux of the gas moving into the oil through the interface can be obtained from Eq.(6). Differentiate Eq.(6) by  $y$  and substitute 0 for  $y$ . Then

$$\left( \frac{\partial C}{\partial y} \right)_{y=0} = -\alpha \left\{ P(s) - \frac{p_i}{s} \right\} \sqrt{\frac{s}{\kappa}} \tanh \left( l \sqrt{\frac{s}{\kappa}} \right) \quad (7)$$

Inversely transforming Eq.(7) to the time domain yields

$$\begin{aligned} \left( \frac{\partial c}{\partial y} \right)_{y=0} &= \frac{\alpha}{\sqrt{\pi \kappa}} \left[ \frac{p_i - p(0)}{\sqrt{t}} \left\{ 1 + 2 \sum_{m=1}^{\infty} (-1)^m \exp \left( -\frac{m^2 l^2}{\kappa t} \right) \right\} \right. \\ &\quad \left. - \int_0^t \frac{dp}{d\tau} \frac{1}{\sqrt{t-\tau}} \left\{ 1 + 2 \sum_{m=1}^{\infty} (-1)^m \exp \left( -\frac{m^2 l^2}{\kappa(t-\tau)} \right) \right\} d\tau \right] \quad (8) \end{aligned}$$

Since the depth of the oil  $l$  is chosen to be 0.1 m, the time  $t$  is 10 hours (36000 s) at the maximum and  $\kappa$  has the order of  $10^{-9}$  m<sup>2</sup>/s in the real measurement, the exponential terms in Eq.(8) are negligibly smaller than 1. Consequently, via

Fick's law, the changing rate of the gas mole number  $dn/dt$  is related to the pressure  $p(t)$  as follows:

$$\frac{dn}{dt} = A\kappa \left( \frac{\partial c}{\partial y} \right)_{y=0} = \frac{A\alpha\sqrt{\kappa}}{\sqrt{\pi}} \left\{ \frac{p_i - p(0)}{\sqrt{t}} - \int_0^t \frac{dp}{d\tau} \frac{1}{\sqrt{t-\tau}} d\tau \right\} \quad (9)$$

The above expression shows that the rate of gas dissolution into an oil is proportional to a product of the reciprocal Henry's constant  $\alpha$  and the square root of the diffusion coefficient  $\sqrt{\kappa}$ . When Eq.(9) and the equation of state, which gives another relation between the pressure and the mole number, are simultaneously solved, the time profile of the pressure change is theoretically determined.

As an equation of state, the perfect gas law (Boyle-Charles' equation)

$$pV = nRT \quad (10)_1$$

is used for  $N_2$  and  $O_2$ , whereas van der Waals' equation

$$\left( p + a \frac{n^2}{V} \right) (V - bn) = nRT \quad (10)_2$$

is adopted for  $CO_2$ . From Eq.(9) and either of Eqs.(10)<sub>1</sub> and (10)<sub>2</sub> where  $V$  and  $T$  are constant, the differential equation to determine the pressure profile is derived. In the cases of  $N_2$  and  $O_2$ , for example, the equation becomes

$$\frac{dp}{dt} = \varepsilon \left\{ \frac{p_i - p(0)}{\sqrt{t}} - \int_0^t \frac{dp}{d\tau} \frac{1}{\sqrt{t-\tau}} d\tau \right\} \quad (11)$$

where

$$\varepsilon = \frac{ART\alpha\sqrt{\kappa}}{V\sqrt{\pi}} \quad (12)$$

Then numerically calculating Eq.(11) gives the pressure  $p(t)$ , the profile of which solely depends on the parameter  $\varepsilon$ .

Although the gas mole number is assumed to change instantaneously at  $t = 0$  in the above analysis, that cannot be true in a real situation. It inevitably takes some finite time  $t_0$  until the change of the gas mole number is completed and the consequent temperature fluctuation has settled down. Therefore Eq.(11) is an approximation only when the settling time  $t_0$  is very small. In order to minimize the errors caused by this discrepancy, the experimental data of the transient pressure change up to  $t = t_0$  is incorporated into the model calculation.

Equation (9) is correct for any  $t \geq 0$ , whereas the equation of state must be applied only for  $t \geq t_0$ . Besides  $p_i = p(0)$  in the real test, because the actual pressure change cannot be discontinuous. In consequence the following equation takes the place of Eq.(11).

$$\frac{dp}{dt} = -\varepsilon \left\{ \int_0^{t_0} \frac{dp}{d\tau} \frac{1}{\sqrt{t-\tau}} d\tau + \int_{t_0}^t \frac{dp}{d\tau} \frac{1}{\sqrt{t-\tau}} d\tau \right\} \quad (t \geq t_0) \quad (13)$$

The first term in the right hand braces in Eq.(13) is a correction to the discrepancy between the theoretical model and the experimental one at the initial transient stage  $0 \leq t \leq t_0$ , and is evaluated from the experimental pressure data.

Finally the diffusion coefficient  $\kappa$  is determined through the process of optimally fitting the pressure profile calculated by Eq.(13) to the measured one. To avoid being subjective, the least squares method is introduced to find the most appropriate value of  $\varepsilon$ .

### 3. MEASUREMENT OF SATURATED GAS SOLUBILITIES

As a prerequisite to applying the above-described one-dimensional diffusion process to the measurement of gas-oil diffusivity, it needs to be experimentally examined whether Henry's law is really true between the gas and oil used for the present test. For that purpose saturated solubilities of the test gases ( $N_2$ ,  $O_2$ ,  $CO_2$ ) into the test oils (Table 1, VG10 commercial machine oil and its bases supplied by Idemitsu Kosan Co., Ltd.) are measured under several different pressures.

#### 3.1 Apparatus and method

Figure 2 diagrammatically shows the configuration of the apparatus; two vessels A and B (inner volumes  $V_A=388 \pm 2.0 \text{ cm}^3$ ,  $V_B=87.5 \pm 1.0 \text{ cm}^3$ ), the gas cylinder and the vacuum pump are connected by pipes with a shut-off valve in between. Both vessels A and B are submerged in a water bath whose temperature is regulated to remain constant within  $\pm 0.1^\circ\text{C}$ . A thermistor ( $\pm 0.1^\circ\text{C}$  in accuracy) and an absolute pressure transducer of a strain gauge type (rated pressure range: 2 MPa.Abs, linearity: 0.04 %) are mounted on the lids of the vessels A and B, respectively, to constantly monitor the temperature and pressure of the confined gas.

In the first place a certain amount of test oil which has been precisely weighed in advance by an electronic balance is put in the vessel A. Its exact volume  $V_O$  at the test temperature is accurately determined from the preliminarily measured density-temperature relation of the oil (possible errors less than 0.1 %). After the vessel is airtightly capped with a lid, the oil is deaerated by a vacuum pump while being stirred by the electro-magnetically driven rotor. When the oil is completely degassed, valve a is closed. Subsequently vessel B is filled with the test gas supplied from the cylinder and valve b is also closed. Some time later when equilibrium has been reached in both vessels, the pressure ( $p_1$ ) is recorded to find the mole number of the gas ( $n_1$ ) enclosed in vessel B. Then valve a is opened to let the gas move into vessel A, where the magnetic rotor stirs the oil to enhance solution. Three hours later when the rate of pressure change is less than 0.2 kPa/hour, it is estimated that the pressure ( $p_2$ ) becomes constant and the oil has been saturated with the gas. The mole number of the undissolved gas  $n_2$  at this point is calculated by the equation of state with the gas volume  $V_G = V_A + V_B - V_O - V_S$  and the pressure  $p_2$ . In consequence the saturated molar concentration  $c_S$  of the test gas at the pressure  $p_2$  is determined by

$$c_S(p_2) = \frac{n_1 - n_2}{V_O} \quad (14)$$

The procedure is repeated under different start-up pressures ( $p_1$ ) with the same test oil maintained in vessel A.

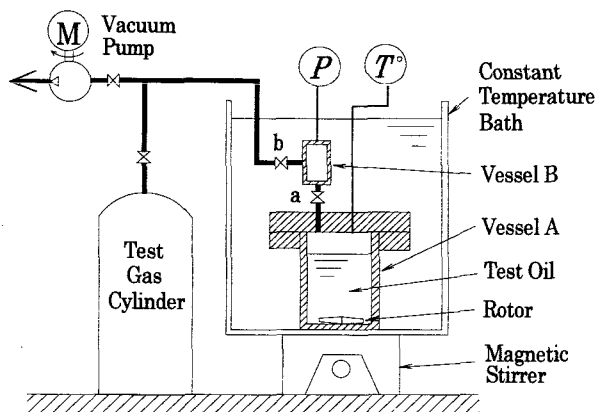


Fig.2 Apparatus for saturated solubility measurement

Table 1 Mineral oils used for test

Oil	Features
I	On-the market VG10 mineral oil
II	Base oil without aromatic compounds
III	Base oil with aromatic compounds
IV	III + additives

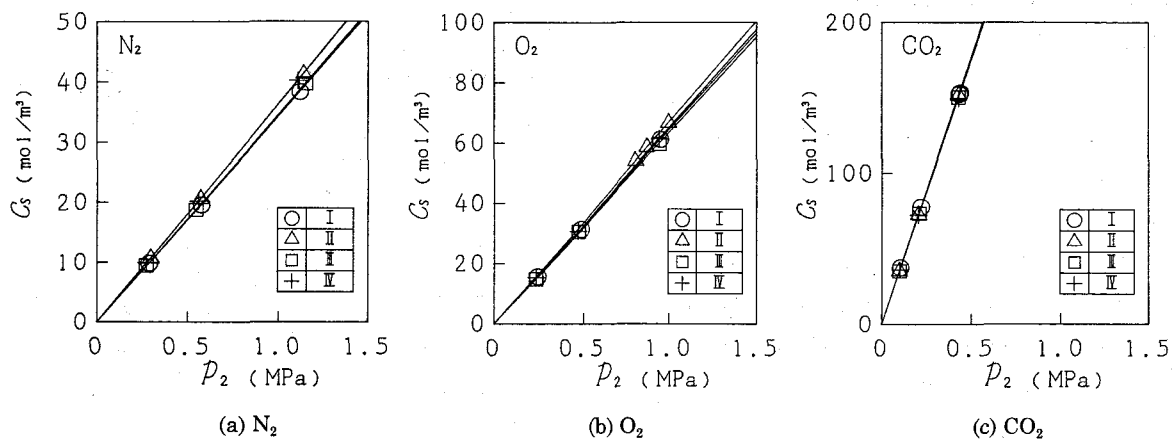


Fig.3 Results of saturated solubility measurements

### 3.2 Results and discussions

The experimental results for the three test gases are plotted in Fig.3 (a) to (c) with the pressure  $p_2$  and the saturated molar concentration  $c_s$  taken on the abscissa and ordinate, respectively. Each figure contains the results for 4 different kinds of test oils (Table 1) at the same temperature (40°C). The straight lines represent Henry's law determined by the least squares method, and their gradients ( $\alpha$ ) are shown in Table 2.

It is apparent from Fig.3 that Henry's law precisely holds true between the three gases and four oils tested and that the same gas has almost the same Henry's constant even for the different oils. Moreover  $O_2$  dissolves into the oil about twice as much as  $N_2$  under the same pressure, while  $CO_2$  does about ten times as much. Naturally it leads to an estimation that a mineral oil long exposed to the atmosphere dissolves  $N_2$  and  $O_2$  by the molar ratio of about 2:1. Therefore it is not proper to say that this kind of oil contains "air", as far as the  $N_2$ - $O_2$  molar ratio is concerned.

Similar measurements have been carried out at several different temperatures. In Fig.4  $\alpha$ 's thus obtained with the test oil I are plotted against the temperature; the saturated solubilities of  $N_2$  and  $O_2$  scarcely vary with the temperature, whereas that of  $CO_2$  evidently decreases with an increase in temperature.

In Figs.3 and 4 there are good agreements between the experimental data and their LSM evaluations. In addition the scattering of the data is small enough, indicating that the experiments have been precisely executed. However, this precision does not necessarily support the quantitative accuracy, though it may indicate the reliability of the pressure measurement and temperature control. That is because the volume of the vessel chamber, with which the gas mole number is calculated by the equation of state, can only be determined with some uncertainty owing to its complicated

Table 2 Reciprocal Henry's constants ( $\times 10^{-5} \text{ mol}/(\text{m}^3 \cdot \text{Pa})$  @40°C)

Oil	$N_2$	$O_2$	$CO_2$
I	3.42	6.44	35.2
II	3.62	6.70	35.4
III	3.45	6.34	35.3
IV	3.63	6.51	35.0

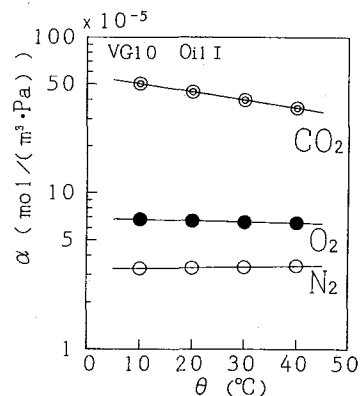


Fig.4 Dependency of reciprocal Henry's constants on temperature

shape. Thereby obtained  $\alpha$  inevitably includes some systematic error estimated below.

With Eqs.(10)<sub>1</sub> and (14)  $\alpha$  is expressed by

$$\alpha = \frac{1}{V_O RT} \left\{ \left( \frac{p_1}{p_2} - 1 \right) V_B - V_A + V_O + V_S \right\} \quad (15)$$

The systematic error  $\Delta\alpha$  resulting from the volumetric errors  $\Delta V_A$  and  $\Delta V_B$  is assessed by Eq.(15) as

$$\frac{\Delta\alpha}{\alpha} \leq \frac{\left| \left( \frac{p_1}{p_2} - 1 \right) \Delta V_B \right| + |\Delta V_A|}{\left| \left( \frac{p_1}{p_2} - 1 \right) V_B - V_A + V_O + V_S \right|} \quad (16)$$

With the present apparatus  $\Delta V_A$  and  $\Delta V_B$  are estimated as 2 and 1 cm<sup>3</sup>, respectively, at the most. Thus, the maximum relative errors in  $\alpha$  are estimated to be 8.5, 5.2 and 1.9 % for N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub>, respectively, at 40°C.

#### 4. MEASUREMENT OF DIFFUSION COEFFICIENTS

##### 4.1 Apparatus and method

Figure 5 gives an illustration of the apparatus designed to bring the present idea of measuring diffusivity into practice. The cylindrical test vessel A and the gas reservoir B are placed in a constant temperature bath. These vessels and the other elements, which are the deaeration vessel C, the level gauge D, a vacuum pump and a gas cylinder, are connected to each other by pipes having a shut-off valve in between.

The first step of the measurement is to put a test oil in the deaeration vessel C and completely degas it by means of the vacuum pump and magnetic rotor. Subsequently the test vessel A, the level gauge D, the gas reservoir B and the connecting pipes are all evacuated. Valve c is opened, and the degassed oil is pushed into the level gauge D as well as into vessel A using the piston installed in the deaeration vessel C. Then the valves a, b and c are closed, reservoir B is filled with the test gas at a specific pressure and valve d is also closed.

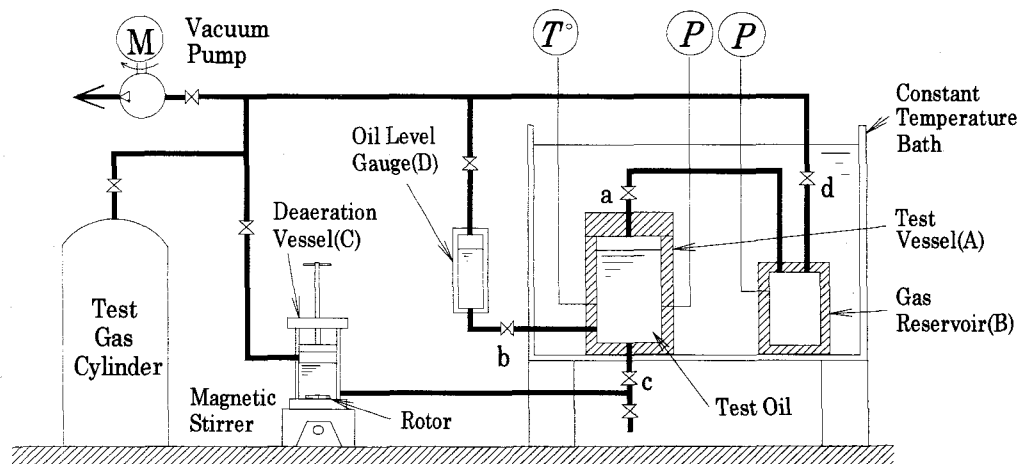


Fig.5 Apparatus for diffusion coefficient measurement

After enough time elapses until both the oil in vessel A and the gas in reservoir B attain the same temperature as the water bath, valve a is opened and the gas is discharged from reservoir B into vessel A. The gas passage in vessel A has been made to prevent the discharging gas from forming a jet which can splatter the oil surface. The pressure measurement starts at this moment with the absolute pressure transducer of a resistance wire strain gauge type (rated pressure range: 0.5 MPa.Abs, linearity: 0.08 %). When the steep pressure change at the initial transient stage has settled down, valve a is closed. The measurement continues thereafter for about 10 hours, during which the oil temperature is monitored by the thermistor mounted on vessel A. After the measurement is over, the lid is removed and the depth of the oil is measured to find the oil and gas volumes in vessel A.

Ahead of the real test, vessel A was filled with nitrogen at 0.5 MPa.Abs to check its airtightness. When the pressure was observed for a sufficient time, the rate of the pressure decrease turned out to be less than 0.1 kPa/hour, which can be regarded as a satisfactory level of sealing for the present purpose.

#### 4.2 Results

The 10-hour pressure profiles experimentally obtained for N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> with the test oil I are reproduced in Figs.6 (a) to (c), respectively, by solid lines. The broken lines show the theoretical calculations optimally fitted to the experimental values.

Obviously there is close agreement between the measurements and the theoretical fittings with N<sub>2</sub> and O<sub>2</sub>. With CO<sub>2</sub>, however, that is not the case, which suggests that not all the assumptions in Section 2 are valid for CO<sub>2</sub>. Although it is difficult as of now to specify which one is not, the assumption (ii) that the diffusion coefficient is independent of the pressure may become questionable in the case of CO<sub>2</sub>, considering that the pressure change through the test is much larger for CO<sub>2</sub> than for N<sub>2</sub> and O<sub>2</sub>.

All the measurements carried out at different starting pressures using the test oils I and II showed that the relationships between the experimental results and the theoretical fittings are almost the same as the ones exhibited in Fig.6, not only for N<sub>2</sub> and O<sub>2</sub> but for CO<sub>2</sub> as well.

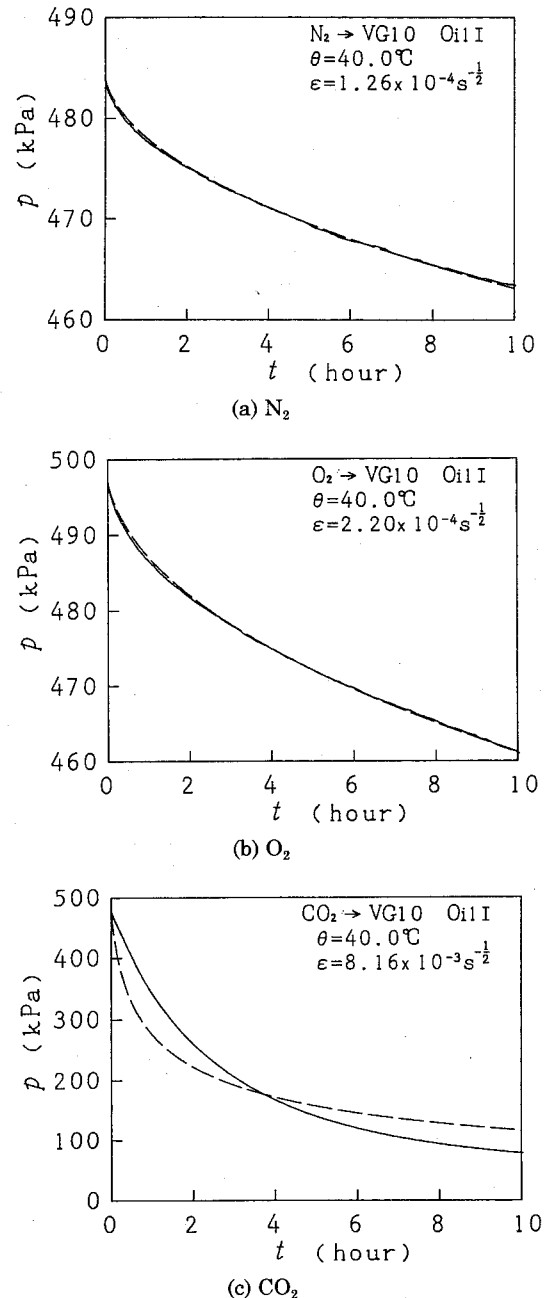


Fig.6 Pressure profile data (solid line) and optimally fitted calculations (broken line)



Table 3 Results of diffusion coefficient measurements (@ 40°C)

		(a) N <sub>2</sub>								
No.		1	2	3	4	5	6	7	8	9
	$V$ (cm <sup>3</sup> )	2.39	2.90	2.69	3.75	4.14	4.51	2.87	4.22	4.43
Oil I	$\sigma$ (kPa)	0.252	0.167	0.098	0.108	0.174	0.120	0.207	0.227	0.161
	$\kappa$ ( $\times 10^9$ m <sup>2</sup> /s)	1.14	1.34	1.57	1.08	1.01	0.97	0.99	1.11	1.41

No.		1	2	3	4	5
	$V$ (cm <sup>3</sup> )	2.87	3.67	3.24	2.79	3.71
Oil II	$\sigma$ (kPa)	0.301	0.240	0.307	0.297	0.288
	$\kappa$ ( $\times 10^9$ m <sup>2</sup> /s)	1.41	1.42	1.27	1.27	0.98

		(b) O <sub>2</sub>					
No.		1	2	3	4	5	6
	$V$ (cm <sup>3</sup> )	2.54	3.22	4.80	5.70	2.60	3.90
Oil I	$\sigma$ (kPa)	0.319	0.235	0.237	0.468	0.534	0.339
	$\kappa$ ( $\times 10^9$ m <sup>2</sup> /s)	1.44	1.41	1.44	1.31	1.40	1.14

No.		1	2	3	4	5
	$V$ (cm <sup>3</sup> )	2.69	12.57	3.32	3.96	3.43
Oil II	$\sigma$ (kPa)	0.369	0.170	0.284	0.211	0.210
	$\kappa$ ( $\times 10^9$ m <sup>2</sup> /s)	1.52	2.30	1.52	1.42	2.35

### 4.3 Diffusion coefficients and their uncertainties

Substituting  $\varepsilon$  found in the fitting process,  $\alpha$  measured in Section 3 and also the data of  $A$ ,  $T$  and  $V$  into Eq.(12) gives the diffusion coefficient  $\kappa$  for N<sub>2</sub> and O<sub>2</sub>. The obtained values of  $\kappa$  are tabulated in Table 3, together with the gas volume  $V$  and the standard deviation  $\sigma$  of the pressure data around the optimally fitted theoretical pressure profile.

The values of  $\kappa$  at the same temperature vary substantially even for the same combination of the oil and the gas, indicating that the present method has its own limit of reliability; for the marketed oil I the deviations of  $\kappa$  around its arithmetic mean lie between +33% and -18% with N<sub>2</sub>, or between +7% and -16% with O<sub>2</sub>, while for the base oil II they lie between +12% and -23% with N<sub>2</sub>, or between +29% and -22% with O<sub>2</sub>. It also turned out that the differences of  $\kappa$  between N<sub>2</sub> and O<sub>2</sub> are much smaller than those of  $\alpha$ . Moreover the diffusion coefficients of N<sub>2</sub> and O<sub>2</sub> obtained here are about 2 to 5 times larger than those of "air" previously measured by the conventional bubble method [4-7], although it

needs to be noted that the oils used in both cases were different.

In the present method, the possible factors that bring errors into the results of  $\kappa$  are the gas volume  $V$ , the reciprocal Henry's constant  $\alpha$ , the pressure measurement and gas leakage. However, errors in  $\alpha$  are much more systematic than accidental as stated before. Among the other three the uncertainty of the volume  $V$  is suspected as being a major cause of accidental errors in  $\kappa$ .

An additional aim of the study is to find how the diffusion coefficient depends on the temperature. One previous report says that the diffusion coefficient of air to an oil roughly doubles when the temperature rises by 30 °C<sup>(7)</sup>. However the diffusion coefficients discovered in the present measurement did not vary that much with the temperature. Figure 7 gives an example of  $\kappa$  measured at 10 and 40°C with N<sub>2</sub> and the base oil II. Obviously the variations of  $\kappa$  after a 30°C temperature rise remain within the experimental uncertainties of the present method.

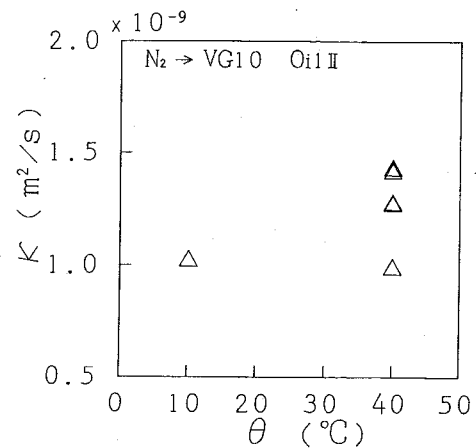


Fig.7 Diffusion coefficients at different temperatures

## 5. DISCUSSIONS ON DIFFUSION PROCESS OF MIXED GAS BUBBLE IN OIL

Since hydraulic oil used in engineering is usually exposed to the atmosphere, it naturally contains some mixed gas, which is traditionally called "air". When gas-liquid diffusion about a bubble in a hydraulic oil is discussed, it used to be a common attitude to assume that the dissolved mixed gas has its own characteristic values of saturated solubility and diffusion coefficient<sup>(4-7)</sup>. The analysis based on that premise is named "single gas analogy" here for convenience.

When a mixed gas is composed of N<sub>2</sub> and O<sub>2</sub> with a molar ratio  $\gamma$ , its apparent saturated solubility  $c_{N+O}$  to an oil is given by Dalton's law as

$$c_{N+O} = \frac{\gamma\alpha_N + \alpha_O}{1 + \gamma} p \quad (17)$$

where  $p$  is the total gas pressure. If the mixture ratio  $\gamma$  is kept constant, which is the case of the atmosphere, Eq.(17) indicates that Henry's law is true with the mixed gas. When the mixed gas is confined inside a bubble in an oil, however,  $\gamma$  inevitably changes at every moment throughout the diffusion process, because N<sub>2</sub> and O<sub>2</sub> have different solubilities and different diffusion rates to the oil. In that case the molar ratio  $\gamma$  varies with the pressure  $p$ , which means Eq.(17) no longer represents Henry's law.

Rigorously speaking, there is no reason to believe that a mixed gas has its own diffusion coefficient or obeys diffusion theory. There are just individual diffusions of each component gas which obeys diffusion theory, and diffusion of a mixed gas must be analyzed as the sum of those individual diffusions (called "rigorous analysis" hereafter).

Now an imaginary example is introduced to clarify the point at issue; a minute spherical bubble (0.3 mm diameter) containing N<sub>2</sub> and O<sub>2</sub> at 4 : 1 molar ratio suddenly emerges at  $t=0$  in the completely degassed oil I under a constant

pressure (101.3 kPa) and its center stays at the same position thereafter (the buoyancy is neglected). Calculating the spherically symmetric diffusion equation including the transportation term by the finite difference method<sup>(8)</sup> gives variations of the bubble radius, the gas mixture ratio and the gas concentrations on the surface with time. In rigorous analysis, the diffusion coefficients ( $\kappa_N=1.17 \times 10^{-9} \text{ m}^2/\text{s}$ ,  $\kappa_O=1.35 \times 10^{-9} \text{ m}^2/\text{s}$ ) and the reciprocal Henry's constants (Table 2) are borrowed from the present measurements. Moreover the surface tension of the oil required in the analysis is chosen as 0.025 N/m.

The results obtained by rigorous analysis are shown in Fig.8 by the solid lines with the time  $t$  on the abscissa; from top to bottom, the bubble radius  $\lambda$ , the molar fraction of  $\text{N}_2$ , and the molar concentrations on the bubble surface  $c_N$ ,  $c_O$  are drawn. On the other hand the broken line in the top figure indicates single gas analogy fitted best to the rigorous bubble radius curve by the least squares method; in that calculation the saturated solubility of the mixed gas was given by Eq.(17) with  $\gamma=4$ . As a result of the fitting, the diffusion coefficient  $\kappa_{N+O}$  of the mixed gas was found to be  $1.09 \times 10^{-9} \text{ m}^2/\text{s}$ .

Figure 8 supports the contention that a mixed gas in a bubble can by no means be regarded as a single component gas in terms of diffusion. When a mixed gas is "air", though, the differences between the results derived by rigorous analysis and those by single gas analogy are usually too small to be experimentally distinguished. That is because  $\text{N}_2$  is the major component of air and also because another component  $\text{O}_2$  has a diffusion coefficient value close to that of  $\text{N}_2$ . Under the circumstances single gas analogy probably has long been relied upon to study air bubbles in an oil. The diffusion coefficients of air to oils so far obtained by the combination of the "bubble" method and single gas analogy vary by several times and are about 2 to 5 times larger than the ones of  $\text{N}_2$  and  $\text{O}_2$  measured in the present paper<sup>(4,7)</sup>.

## 6. CONCLUSIONS

The saturated solubilities and diffusion coefficients of nitrogen, oxygen and carbon dioxide to mineral oils have been measured. The findings are as follows:

- (1) The reciprocal Henry's constants of  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CO}_2$  to a VG 10 machine oil are 3.42, 6.44 and  $35.2 \times 10^{-5} \text{ mol}/\text{m}^3 \cdot \text{Pa}$ , respectively, at  $40^\circ\text{C}$ . It means that  $\text{O}_2$  and  $\text{CO}_2$  dissolve in the oil about 2 and 10 times as much as  $\text{N}_2$ , respectively.
- (2) The method proposed in the present paper to measure diffusion coefficients between a gas and an oil has proved effective. The diffusion coefficients of  $\text{N}_2$  and  $\text{O}_2$  obtained by the method are 1.17 and  $1.35 \times 10^{-9} \text{ m}^2/\text{s}$ , respectively, on the

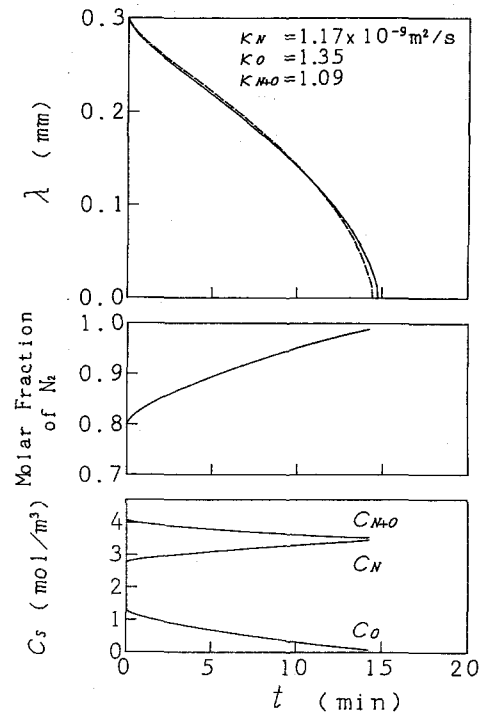


Fig.8 Comparison of single gas analogy with rigorous analysis regarding diffusion behavior of mixed gas bubble in oil

average, and scatter between +33% and -18% around the average for  $N_2$ , and also between +7% and -16% for  $O_2$ .

(3) In the case of  $CO_2$ , it was unattainable to theoretically simulate the experimental data of the pressure variation and therefore to obtain the diffusion coefficient for the gas. One possible explanation for this failure is the pressure changes so dramatically for  $CO_2$  that the dependency of the diffusion coefficient on the pressure becomes no more negligible, contrary to the assumption adopted in the theoretical model.

(4) There are few noticeable differences between the marketed oil and its base oils with respect to the saturated solubilities and diffusion coefficients.

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