

DIFFUSION OF GASES IN LIQUIDS. II.\*  
DISSOLUTION OF A STATIONARY GAS  
BUBBLE IN A LIQUID

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A new solution is given to the problem of the diffusion controlled dissolution of a gas bubble in a liquid, obtained by a finite difference method with an implicit computational scheme. It has been established that  $\beta \cdot T^* = 1.32$  holds for  $\beta$  parameter from the interval  $\beta \leq 0.2$ . This result can be utilized for the calculation of the diffusion coefficient of a gas in a given liquid from the dissolution time of a bubble of a known initial size. A value  $D = 9.87 \cdot 10^{-5} \text{ cm}^2/\text{s}$  (25°C, 1 atm), obtained in this manner for hydrogen-tetrachlormethane system, was compared with those, resulting from other methods of evaluation of time dependences of the bubble size. The obtained value of the diffusion coefficient for the mentioned system agrees very well with an earlier published value determined by an entirely different technique.

The method of dissolution of a stationary gas bubble in a liquid with a uniform initial concentration of the dissolving gas has been used to determine the values of the diffusion coefficient for a number of systems<sup>1-13</sup>. However, no standard routine of evaluation of experimental data has thus far resulted from these works. The evaluation of the diffusion coefficient itself poses a problem of the solution of the following partial differential equation, given in dimensionless form with proper boundary conditions:

$$\left(\frac{\partial C(R, T)}{\partial T}\right) = \left(\frac{\partial^2 C(R, T)}{\partial R^2}\right) + \left(\frac{\partial C(R, T)}{\partial R}\right) \left[\frac{2}{R} + \frac{A^2(T)}{R^2}(\alpha - 1)\beta G(T)\right],$$

$$A(0) = 1; \quad C(R > A, 0) = 0; \quad C(A, T) = 1; \quad \lim_{R \rightarrow \infty} C(R, T) = 0 \quad (1)$$

where

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$$G = \left( \frac{\partial C(A, T)}{\partial R} \right) \quad \text{and} \quad \frac{dA}{dT} = \beta G .$$

This set of equations (1) cannot be solved analytically.

A numerical solution for some values of parameters  $\alpha$  and  $\beta$  was furnished in papers of Ready and Cooper<sup>14</sup>, and Cable and Evans<sup>15</sup>.

For pseudo-stationary case, the partial differential equation (1) can be transformed, together with the boundary conditions, into an ordinary differential equation of the form:

$$dA/dT = -\beta \{1/A + 1/(\pi T)^{1/2}\} , \quad (2)$$

$$A(0) = 1 .$$

A complete solution of this equation was presented by Epstein and Plesset<sup>16</sup> and subsequently used<sup>10</sup> for a nonlinear regression analysis of measured time dependences of the bubble size to obtain values of the diffusion coefficient of the corresponding system. The discussed solution takes following form in our notation:

$$\ln [A^2 + 2\beta A(T/\pi)^{1/2} + 2\beta T] - 2\beta/K \arctan \{K/[\beta + A(\pi/T)^{1/2}]\} = 0 \quad (3)$$

where  $K = (2\pi\beta - \beta^2)^{1/2}$ .

On neglecting  $1/A$  or  $1/(\pi T)^{1/2}$  term in equation (2), two limit solutions are obtained:

$$A = 1 - 2\beta(T/\pi)^{1/2} , \quad (4)$$

$$A^2 = 1 - 2\beta T . \quad (5)$$

The properties of the system studied, *i.e.* the diffusion coefficient and initial radius of the bubble  $a_0$ , determine which of the Eqs (4) and (5) is to be used for analysis of the experimental data. A criterion for this selection is inequality

$$1/A \geq 1/(\pi T)^{1/2} \quad \text{or} \quad (\pi D t/a)^{1/2} \geq 1 . \quad (6)$$

Solution (5) has been applied in most papers dealing with the diffusion of slightly soluble gases in liquids<sup>1-3,6,7,9,13,16</sup>. In all cited papers Eq. (5) agrees well with experimental dependences, primarily in the initial stage of the dissolution process when the interphase motion due to the loss of mass from the bubble is supposedly negligible.

Hlaváč and Němec<sup>17</sup> compared still other theoretical time dependences of the bubble size at dissolution. They found large discrepancies between individual solutions as the curves differed not only in their course but in their shape as well. From theoretical point of view particularly interesting is the work of Duda and Vrentas<sup>18</sup> presenting an approximate solution to the diffusion equation (1) on the basis of perturbation analysis. The results of this approach were compared in the cited paper with authors' own solution by a finite difference method.

The aim of this work is to present a new numerical solution of Eq. (1). The diffusion coefficient of hydrogen in tetrachloromethane, evaluated from experiments using this solution, is compared with its values furnished by other methods of evalua-

tions applied to the same experimental data. The diffusion coefficients for our system are further compared with a value measured by Ross and Hildebrandt<sup>19</sup> using an entirely different experimental method (diaphragm cell). Our own experimental set-up and measuring technique were described in detail in the preceding communication<sup>13</sup>.

#### NUMERICAL SOLUTION OF THE DIFFUSION EQ. (1)

Cable and Evans<sup>15</sup> have published a method of the solution of Eq. (1) in detail. Their results were presented in the form of the dependence of the dimensionless dissolution time  $T^*$  on parameters  $\alpha$  and  $\beta$ . Unfortunately, this paper does not provide enough values of  $T^*$  for low values of the coefficient  $\beta$ , typical for hydrogen-organic solvent systems ( $\beta \leq 0.2$ ;  $\alpha = 0$ ), to which we focussed our attention. This stimulated our attempt for our own solution of Eq. (1). In contrast with the work<sup>15</sup> we used an implicit computational scheme.

Let us denote the spatial increment  $\Delta R$ , time increment  $\Delta T$  and  $C_{i,j}$  the concentration at the point  $i$  and time  $T = j \Delta T$ . Substituting  $R' = R - A$ , which has no effect on the increment  $\Delta R$ , the origin of the computational grid is shifted into the point  $R = A$  for an arbitrary time instant. Since, however, the bubble size  $A$  is a function of time  $T$ , the implemented transform changes the time increment  $\Delta T$  into  $\Delta T'$  according to the relation:

$$\Delta T' = \Delta T [1 + (dA/dT)^2]^{1/2} = \Delta T (1 + \beta^2 G^2)^{1/2}. \quad (7)$$

This fact markedly complicates solution of pertaining difference equations as the gradient at the interphase is generally also a function of time. Considering that we seek a solution in the range of low values of the parameter  $\beta$ , i.e. for cases when the dissolution of the bubble takes place sufficiently slowly, it is possible to take the original, untransformed time increment  $\Delta T$  into computation instead of  $\Delta T'$ , provided that:

$$1 \gg (dA/dT)^2, \quad \text{respectively} \quad 1 \gg \beta^2 G^2. \quad (8)$$

It is obvious that the dissolution times resulting on the basis of this assumption will be somewhat shorter than those, corresponding to Eq. (1).

The computational check-up has shown the value of the square root in equation (7) smaller than 1.01 for  $\beta \leq 0.2$ . The differential operators in Eq. (1) can therefore be replaced by following difference relations<sup>20-22</sup>:

$$\partial C / \partial T = (C_{i,j+1} - C_{i,j}) / \Delta T, \quad (9)$$

$$\partial C / \partial R = (C_{i+1,j+1} - C_{i-1,j+1} + C_{i+1,j} - C_{i-1,j}) / 4\Delta R, \quad (10)$$

$$\partial^2 C / \partial R^2 = (C_{i+1,j+1} + C_{i-1,j+1} - 2C_{i,j+1} + C_{i+1,j} + C_{i-1,j} - 2C_{i,j}) / 2\Delta R^2. \quad (11)$$

In this way a following linear, tridiagonal set of equations with respect to  $C_{i,j+1}$  is obtained:

$$\begin{aligned} (2 + 2/\varrho) C_{i,j+1} - (1 - P_{i,j}) C_{i-1,j+1} - (1 + P_{i,j}) C_{i+1,j+1} = \\ = (-2 + 2/\varrho) C_{i,j} + (1 - P_{i,j-1}) C_{i-1,j} + (1 + P_{i,j-1}) C_{i+1,j}, \end{aligned} \quad (12)$$

where  $\varrho = \Delta T/(\Delta R)^2$

$$P_{i,j} = (\Delta R/2) (A_j + i \Delta R)^{-2} [2A_j + 2i \Delta R + A_j^2(\alpha - 1) \beta G_{j+1}].$$

The concentration gradient at the interphase  $G_j$  was replaced, in the set (12), by the following three point approximation formula:

$$G_j = (2 \Delta R)^{-1} (4C_{1,j} - C_{2,j} - 3). \quad (13)$$

The set of difference equations (12) was solved by an iteration procedure using a modified algorithm<sup>23</sup>. Whenever the concentration in the last point of the grid exceeded  $10^{-8}$ , the number of grid points, and consequently the number of equations, was increased by one. Two iterations on average were necessary to achieve the relative error of the resultant gradient  $G_{j+1}$  less than  $10^{-4}$ . Further enhancement of the computational accuracy of the solution of the set (12) had no appreciable effect on the calculated dissolution time  $T^*$ . The computational scheme was completely stable for  $\varrho \leq 1$ . In the range  $1 < \varrho \leq 20$ , the values of the gradient and concentrations in individual points oscillate at the beginning of the computation. This phenomenon, however, has no effect on the dissolution time  $T^*$ . The accuracy of the solu-

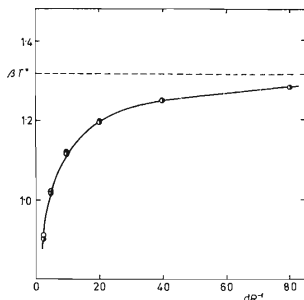


FIG. 1  
Dependence of Product  $\beta T^*$  on Inverse  
of Radial Increment  $\Delta R$   
 $\circ \beta = 0.08$ ,  $\bullet \beta = 0.2$ .

tion was examined for two different values of the coefficient  $\beta$  ( $\beta = 0.08$  and  $\beta = 0.2$ ) and for  $\alpha = 0$ . The computation was performed using different increments  $\Delta R$ . It is apparent that diminishing increment will yield more accurate results. The appropriate time increment was determined from the quantity  $\varrho$ , coupling both increments by above mentioned condition (for  $\varrho > 20$  solution of (12) diverges).

Figure 1 plots the product of the dimensionless dissolution time  $T^*$  and coefficient  $\beta$  in the dependence on the inverse of the increment  $\Delta R$ . Figure shows clearly that with vanishing increment  $\Delta R$ , the product  $\beta T^*$  does not depend practically on the coefficient  $\beta$ , and its value, for  $\Delta R^{-1} = 80$ , sufficiently approximates the limiting solution for  $\Delta R \rightarrow 0$  shown by broken line. The limiting value of the product  $\beta T^* = 1.32349$  for this case was obtained by extrapolation of the results using the Lagrangian interpolation polynomial<sup>22</sup>.

## RESULTS AND DISCUSSION

### Results of the Solution of Eq. (1)

The results of the solution of partial differential equation (1) are shown in Fig. 2 as a plot of the dependence of the inverse of the dimensionless time  $T^*$  on the parameter  $\beta$ . The dependence obtained by an implicit computational scheme is linear

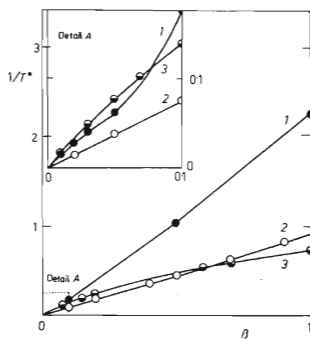


FIG. 2

Dependence of Inverse of Dissolution Time of Bubble  $T^*$  on Coefficient  $\beta$

1 Solution by Cable and Evans<sup>15</sup>, 2 this work, 3 solution according to Eq. (3).

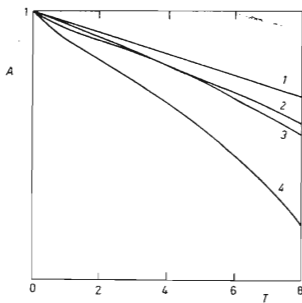


FIG. 3

Time Dependence of Bubble Size

1 This work, 2 solution by Cable and Evans<sup>15</sup>, 3 solution according to Eq. (3), 4 solution by Duda and Vrentas<sup>18</sup>.

in the examined region, which is in agreement with findings of Cable and Evans<sup>15</sup>. The results of these authors (shown also in Fig. 2), however, do not display this property in the range  $\beta < 0.1$ , as can be seen from the detail in Fig. 2. In addition, the numerical values of compared solutions do not agree either. Cable and Evans<sup>15</sup> results of the dissolution time  $T^*$  are approximately one half of those, obtained in this work, while the presented solution is somewhat lower than the accurate solution with respect to the above introduced assumption about the transform. It is very difficult to assess the reason for this discrepancy. It may have been brought about by the explicit computational scheme used in the work<sup>15</sup>, which is usually very sensitive to different instabilities of the solution, or due to the inaccuracy of the interpolation formula applied to the gas-liquid interphase. Interpolation was eliminated in this work by a suitable transform of coordinates at the interphase.

Results presented in Fig. 2 cover the range of  $\beta$  parameter  $\beta \in \langle 0.1 \rangle$ , although for higher values of this parameter, the transform of the origin of coordinates used here is less justified (the value of the square root in Eq. (7) is 1.06 and 1.25 for  $\beta = 0.5$  and  $\beta = 1$  respectively). Nevertheless, the theoretical dissolution time in this case is substantially higher than that, given by Cable and Evans<sup>15</sup>. An analogous dependence for a pseudo-stationary case, obtained by the solution of the transcendent Eq. (3) with respect to  $T$ , for  $A = 0$ , is shown for comparison in the same figure. An elsewhere published<sup>24</sup> algorithm was used to facilitate computation.

Typical courses of time dependences of the size of the dissolving bubble, for  $\beta = 0.05$  and  $\alpha = 0$ , are shown for illustration in Fig. 3. In addition to the above compared solutions, a solution according to Duda and Vrentas<sup>18</sup>, assuming the fastest dissolution of all thus far published papers, is plotted in the same figure. This brings up a question of whether additional terms should not be taken into consideration in the perturbation series of this work<sup>18</sup>, and whether a suitable transform of coordinates was used in authors' own<sup>18</sup> numerical solution verifying the justification of the perturbation approach.

#### *Methods of Evaluation of the Diffusion Coefficient*

In experimental measurements of time dependences of the bubble size, the actual dissolution time is the most accurately measurable quantity. It seems therefore suitable to use this quantity for evaluation of the diffusion coefficient. Furthermore, the initial bubble size has to be known. In the case of a study of diffusion of gases in liquids, approximate solutions (*e.g.* Eq. (5) or (4)) can be made use of with advantage to extrapolate experimental data to zero time, provided that the first experimental point is no too far from the beginning of the dissolution process. A new construction of the measuring cell, described in the preceding communication<sup>13</sup>, enabled to cut this interval down to 10–15 s.

If the condition of spherical symmetry of the concentration field around the bubble,

usually disturbed by the walls of the cell, is not fulfilled, an appropriate correction is necessary. The majority of authors uses a correction suggested by Liebermann<sup>3</sup>. There is some uncertainty as to whether the driving force of the process, *i.e.* the coefficient  $\beta$  ( $\beta = \beta'/\ln 2$ ), or, the resultant diffusion coefficient ( $D = D'/\ln 2$ ) should be corrected. As the solution of the set (1) leads to a linear relation between the inverse of the dimensionless dissolution time and the coefficient  $\beta$ , both corrections necessitate the same result. Similar situation occurs in graphical evaluation of experiments according to Eq. (5), used by majority of authors. In contrast, a non-linear regression, according to Eq. (3), suggested by Krieger, Mulholland and Dickey<sup>10</sup> renders both corrections considerably different (see Table I). Program for a digital computer was prepared on the basis of a general minimizing algorithm used for complex kinetic data processing<sup>25</sup>.

TABLE I  
Comparison of Diffusion Coefficients

Method	Solution (Eq.)	Method of evaluation	$D \cdot 10^5$ $\text{cm}^2 \text{s}^{-1}$	Note
Diaphragm	—	—	9.75	see work <sup>19</sup>
Bubble dissolution	(5)	graphical	10.5	see work <sup>13</sup>
Bubble dissolution	(1) this work	from bubble dissolution time	9.87	—
Bubble dissolution	(1) work <sup>15</sup>	from bubble dissolution time	4.75	—
Bubble dissolution	(3)	regression analysis	10.6	$D = D'/\ln 2$
Bubble dissolution	(3)	regression analysis	5.36	$\beta = \beta'/\ln 2$

The mean values of the diffusion coefficient of hydrogen in tetrachlormethane (25°C, 1 atm) obtained by different evaluation techniques and applied to the experimental data published in the preceding paper<sup>13</sup>, are summarized in Table I. The values of the diffusion coefficient determined by a method of diaphragm<sup>19</sup> are given there for comparison too. Large scatter of results due to the diversity of evaluation techniques is apparent from this survey. The value of the diffusion coefficient, according to the solution given here, comes closest to that, given by Ross and Hildebrandt<sup>19</sup>, while the diffusion coefficient obtained using Cable and Evans<sup>15</sup> solution is by one half lower. Relatively good result was achieved by a simple graphical technique according to Eq. (5), see preceding communication<sup>13</sup>.

Further values of the diffusion coefficient for hydrogen-organic solvent systems will be presented in the following paper.

The authors wish to thank to Dr V. Koza for his valuable assistance at the solution of Eq. (1).

## LIST OF SYMBOLS

$a$	bubble radius (cm)
$a_0$	initial bubble radius ( $t = 0$ ) (cm)
$A = a/a_0$	dimensionless bubble radius
$C_{i,j}$	dimensionless concentration at the point $i, j$
$C^*$	concentration at interphase ( $\text{g cm}^{-3}$ )
$C_1^\infty$	initial concentration in liquid ( $\text{g cm}^{-3}$ )
$C = C_i/C_i^*$	dimensionless concentration
$D$	diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )
$D'$	uncorrected diffusion coefficient affected by walls of cell ( $\text{cm}^2 \text{s}^{-1}$ )
$G$	concentration gradient (see Eq. (1))
$K$	dimensionless coefficient of Eq. (3)
$P$	dimensionless coefficient of Eq. (12)
$r$	radial coordinate (cm)
$\Delta R$	dimensionless radial increment
$R = r/a_0$	dimensionless radial coordinate
$R' = R - A$	dimensionless radial coordinate
$t$	time (s)
$t^*$	dissolution time of bubble (s)
$\Delta T$	dimensionless time increment
$T = Dt/a_0^2$	dimensionless time
$T^* = Dt^*/a_0^2$	dimensionless dissolution time of bubble
$\bar{V}_i$	partial specific volume of component $i$ ( $\text{cm}^3 \text{g}^{-1}$ )
$\alpha = \rho_B \bar{V}_i$	dimensionless coefficient
$\beta = (C_i^* - C_i^\infty)/\rho_B(1 - C_i^* \bar{V}_i)$	dimensionless coefficient
$\beta'$	dimensionless coefficient affected by walls of cell
$\rho$	dimensionless coefficient of Eq. (12)
$\rho_B$	density of gas in bubble ( $\text{g cm}^{-3}$ )

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