

## Application of a radioactive tracer method for diffusion study in some liquids

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**Abstract.** In this paper a radioactive tracer technique based on sliding cell method developed in our laboratory for the study of diffusion in liquids is presented in detail. This method consists of radioactive and non-radioactive liquid columns of equal length and the radiation detector is placed in a vertical geometry over the diffusion column. Some liquid metals and aqueous electrolyte solutions were studied by this method. The data of liquid metals like mercury and gallium have been analyzed from the point of view of hard sphere model and those of electrolyte solutions from phenomenological theories. Onsager's coefficients  $L_{11}$ ,  $L_{12}$ ,  $L_{22}$  have been calculated from the experimental data and the variation of diffusion with solute concentration has been explained from ion-ion interaction.

**Keywords.** Radioactive tracer; diffusion; electrolytes; liquid metals; Onsager's coefficients.

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### 1. Introduction

In recent years, there have been spectacular developments in the study of diffusion phenomena in liquids both theoretically and experimentally. There have been some developments in the radioactive tracer techniques [Passiniemi (1983)] and the computer simulation techniques have added a new dimension. Inelastic neutron scattering, pulsed NMR techniques, optical measurements and various forms of radioactive tracer techniques, have accumulated data on diffusion phenomena in aqueous solutions of electrolytes and also in liquid metals; a detailed treatment can be found in Tyrrell and Harris (1984). Some of these methods which are widely used involve the measurement of the rate of decay of a concentration gradient which usually has the form of a step function created by forming a sharp boundary between two solutions of different compositions. The light scattering methods and also some radioactive tracer techniques depend on the formation of such a boundary horizontally in a vertical column and one dimensional diffusion takes place along the length of the column. On the other hand several methods do not depend upon the establishment of a macroscopic concentration gradient within the system. These involve the use of a radiation probe (light beam, neutron beam, radio frequency pulse in a magnetic field gradient etc.) which is affected by the translational or rotational movement of the molecules themselves. They are less direct in the sense that a theoretical model of the interaction between the probe and the molecular motion is needed. On the other hand all the radioactive tracer methods utilize two properties of the radioactive

isotopes: 1) they emit radiations which can be easily detected and 2) for most purposes they can be treated equivalent to their non-radioactive counterparts. The radioactive tracer methods can be broadly divided into four categories: diaphragm cell method, sneared boundary, capillary technique and sliding cell method depending on the experimental arrangements. The starting point of all these investigations is, of course, the solution of Fick's second law of diffusion under different boundary conditions. The last three named techniques have been extensively used for the measurement of diffusion coefficients in liquid metals. Erickson *et al* (1974), Changdar (1973), Basu *et al* (1980), Nachtrieb and Petit (1956), Hoffman (1952) measured and analyzed the diffusion coefficients in liquid metals mercury, gallium, sodium, indium, lead etc by these methods. All the above mentioned methods have been utilized for the study of electrolyte solutions as evident from the studies of Mills (1985), Liukkonen *et al* (1976), Halla (1981), Chakraborti and Changdar (1982). The sliding cell method has been used in our laboratory for the study of diffusion and we present in this paper our findings.

## 2. Present investigation

The starting point of the present method of measuring diffusion coefficients in liquids is Fick's second law of diffusion for unidirectional flow

$$\frac{\delta C(x, t)}{\delta t} = D \frac{\delta^2 C(x, t)}{\delta x^2}. \quad (1)$$

The general solution of this equation (obtained by the method of separation of variables, as shown by Crank (1979)) is

$$C(x, t) = \sum_{n=0}^{\infty} (a_n \sin \lambda_n x + b_n \cos \lambda_n x) \exp(-\lambda_n^2 D t). \quad (2)$$

In our experiment, the (non-radioactive) part of the diffusion column is superposed on the (radioactive) part of equal cross sectional area and of concentration  $C_0$  at time  $t = 0$ .

Hence for

$$t = 0, C = C_0 \text{ for } x = 0 \text{ to } x = l_1; C = 0 \text{ for } x > l_1 \text{ to } x = l_1 + l_2$$

and

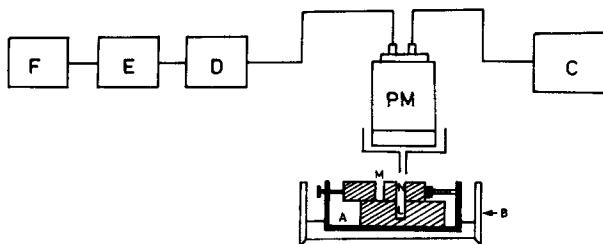
$$\left. \frac{\delta C(x, t)}{\delta x} \right|_{x=0} = \left. \frac{\delta C(x, t)}{\delta x} \right|_{x=l_1+l_2} = 0 \quad (3)$$

and for  $t \rightarrow \infty$ ,  $C = C_0(l_1/l_1 + l_2)$  for all values of  $x$ . These boundary conditions reduce (2) to,

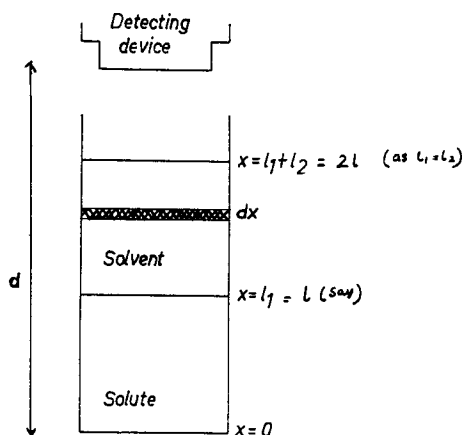
$$C(x, t) = \frac{C_0}{2} + \frac{2C_0}{\pi} \cos\left(\frac{\pi x}{2l}\right) \exp(-kt) \text{ where } k = \frac{\pi^2 D}{4l^2} \quad (4)$$

(neglecting higher order terms and putting  $l_1 = l_2 = l$ ).

In our experimental arrangement (figure 1) the solute is radioactive and the detector is placed vertically over the solute and solvent columns. The count rate observed by



**Figure 1.** Schematic representation of the whole experimental arrangement. A. Diffusion cells and the brass box containing them; B. Insulated double walled box; C. High voltage supply unit; D. Amplifier unit; E. Analyser unit; F. Decade scalar unit; PM. Photomultiplier.



**Figure 2.** Definition of the diffusion column.

the detector is proportional to the integrated weighted average of  $C(x, t)$  over the variables. To evaluate that let us consider an element of layer defined by  $x$  and  $x + dx$  (figure 2). The count rate  $dN(x, t)$  as recorded by the scalar may be written as

$$dN(x, t) = \frac{\varepsilon C(x, t) \phi \{ (2l - x), \mu \}}{\psi(d - x)} \quad (5)$$

where  $\varepsilon$  is a constant representing the overall counting efficiency of the detector,  $\phi(2l - x, \mu)/\psi(d - x)$  is the weight factor involving geometry, absorption and scattering from the layers.

Integrating (5) over the entire range of  $x$ , from  $x = 0$  to  $2l$ ,

$$\Delta N(t) = \varepsilon \int_{x=0}^{x=2l} \frac{C(x, t) \phi(2l - x, \mu)}{\psi(d - x)} dx. \quad (6)$$

Thence

$$N(t) = A_1 - B_1 \exp(-kt) \quad (7)$$

putting (4) into (6), where  $A_1$  and  $B_1$  are independent of time. When the solute and solvent are uniformly mixed, the observed saturation count rate  $N(0)$  equals  $A_1$ . Thus

$$N(0) - N(t) = B_1 \exp(-kt). \quad (8)$$

In actual experiments the counts are recorded for 30 min or 60 min. As this time interval is maintained constant in all subsequent observations, the form of the expression for the observed count rate retains the form of (8). Thus the final working formula can be written as

$$N_0 - N_t = B \exp(-kt) \quad (9)$$

where  $N_0$  is the total saturation count taken over time  $\tau$ ,  $N_t$  is the total count taken at time  $t$  over the same interval  $\tau$ ,  $B$  is a constant. Thus noting integral counts recorded by the detector at finite interval  $\tau$ , and noting the saturation count when the liquid column is completely mixed up mechanically, the diffusion coefficient  $D$  can be evaluated directly from the value of  $k$ .

In our sliding cell arrangement the cells were made of stainless steel and were in the form of rectangular slabs of dimensions  $2.5'' \times 2'' \times 1''$ . The cells sit together, one just above the other, to form the diffusion column proper. The cylindrical cavity of the upper ( $N$ ) and lower ( $L$ ) slab constitute the diffusion column. There is another hole ( $M$ ) in the upper slab for filling the lower hole ( $L$ ) with radioactive solution. The two faces in contact of the pair are polished and ground very carefully. The cell pair is housed in a brass vessel of dimension  $5'' \times 2'' \times 2''$ . The lower slab is kept fixed with respect to the brass vessel with the help of an attaching hook. The upper slab can be slowly slid along the length of the lower one with the help of a screw and a spring, such that the lower surface of it is always in steady contact with the upper surface. This screw and spring arrangement enables to bring the solvent column over the solute column at time  $t = 0$ , i.e. to start the diffusion process. In our experiments we have used cells of diffusion columns ranging from 2 cm to 4 cm having diameters 4 mm to 6 mm.

The process of diffusion is observed throughout the experiment through integral counting over a period of 12–14 h at an interval of 30 min by the detector placed in vertical geometry over the diffusion column. The counting electronics consists of a thin window anthracene crystal coupled to RCA 5819 photomultiplier or NaI(Tl) crystal to 6282 photomultiplier, which is placed just vertically over the diffusion column. The photomultiplier tube was connected in turn to a highly stable electronic circuit consisting of amplifier, analyser and counter-timer. The high voltage supply to the photomultiplier tube was maintained with the help of a regulated power supply unit. The stability of the circuit was checked within  $\pm 1\%$  over a period of 24 h. Proper precautions were taken to minimize mechanical vibration. Temperature was controlled by using a U-10 thermostat.

### 3. Experimental results and discussions

The sliding cell arrangement in our laboratory has been used for tracer diffusion investigations in metallic mercury and gallium and in different electrolyte solutions like thallos sulphate, sodium sulphate, sodium chloride, phosphoric acid, mercuric nitrate etc. using  $^{24}\text{Na}$ ,  $^{32}\text{P}$ ,  $^{204}\text{Tl}$ ,  $^{203}\text{Hg}$ ,  $^{72}\text{Ga}$  as tracers.

#### 3.1 Electrolyte solutions

For experiments with aqueous solutions, first the aqueous solution of the experimental electrolyte is prepared for any chosen concentration by the weighing method. From

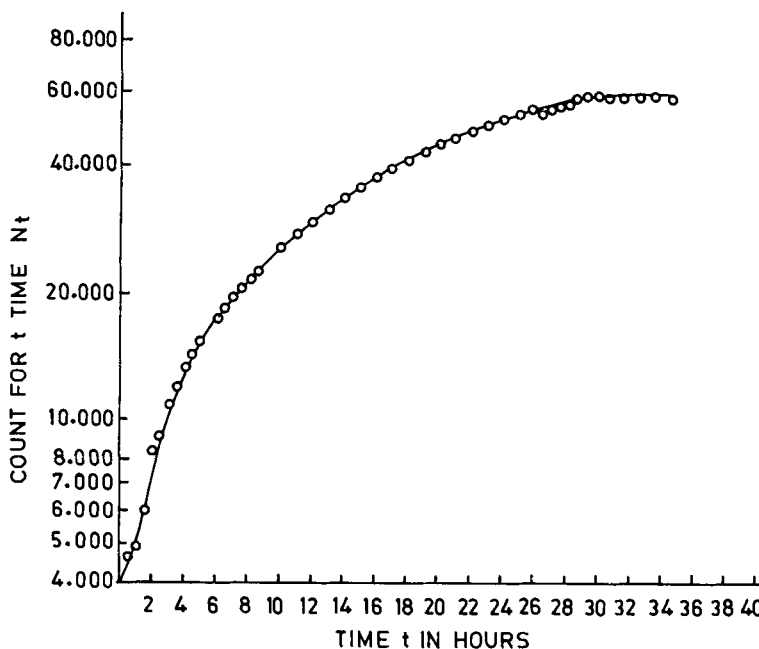


Figure 3. A typical illustration of the instantaneous variation of count rate with time.

this solution, the solute and solvent are prepared; they are same in every respect except the fact that the solute contains the tracer molecules. Initially the lower cavity is filled up with the radioactive solute through the hole (when the upper slab was so placed that  $N$  was just above  $L$ ). The upper hole was then partly filled up with the solvent up to the height equal to the depth of the lower cavity  $L$ . To avoid the evaporation of the liquids from the diffusion column the upper hole  $N$  was covered with a thin polythene piece. At time  $t = 0$ , the solvent column was superposed on the solute column by the sliding screw arrangement. Counting observations ( $N_t$ ) were made after two hours from starting diffusion intervals of half-an-hour ( $\tau = 29$  min). A typical illustration of the instantaneous variation of  $N_t$  with  $t$  is shown in figure 3. At the end of the experiment the system was thoroughly mixed up mechanically after which observation for  $N_0$  was made. The corrected set of  $\ln(N_0 - N_t)$  data for various  $t$  values were analysed by the least square fit procedure to yield the value of  $k$  from which  $D$  is calculated. To get consistent values of  $D$  the experiment is repeated for each particular concentration at least thrice with different diffusion column length and diameters. The experiments were similarly repeated at different temperatures while the diffusion coefficients of mercury and gallium were measured.

The justification for adopting this technique for our investigation lies in the fact that the method is very consistent and accurate. The experimental arrangement and procedure being very simple, there is not much scope for large errors to creep in. The consistency of the method had been checked by measuring the diffusion coefficients at different concentrations for aqueous thallos sulphate solution with  $^{204}\text{Tl}$  as tracer by using our experimental arrangement.

Our data on thallos sulphate solution at limiting concentration may be compared with the diffusion coefficient obtained by Creeth and Peter (1960) and that by Wakeham (1982). While comparing we have to keep in mind that Creeth and Peter

**Table 1.** Diffusion coefficient of sodium ion in aqueous sodium chloride solution at different concentrations at 25°C.

Concentration (C) in mol/dm <sup>3</sup>	Diffusion coefficient $D \times 10^5 \text{ cm}^2/\text{s}$		**Differential diffusion coefficient $D \times 10^5 \text{ cm}^2/\text{s}$
	Obs.	Calc.	
0.0	1.370 <sup>†</sup>	1.334*	1.336
1.0683	0.990	1.057	1.214
1.4239	0.935	1.014	1.202
1.7094	0.908	0.984	1.196
2.4444	0.871	0.915	1.182
3.4188	0.846	0.838	1.172
4.7863	0.760	0.747	1.164
5.6977	0.720	0.694	1.160
6.5520	0.690	0.648	1.156

\* This is Nernst's limiting value of diffusion coefficient.

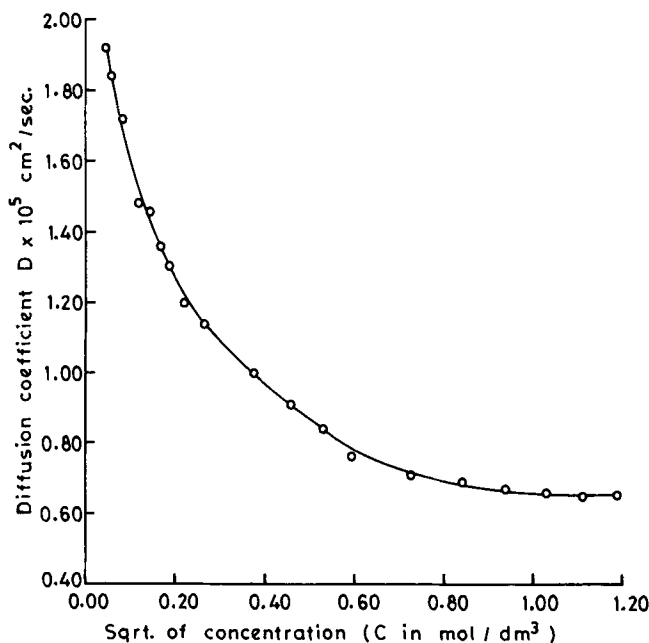
\*\* These values were obtained from the curve of Pentti Passiniemi.

<sup>†</sup> This value was obtained by extrapolating the experimental curve.

studied the electrolyte diffusion by interferometric method and their limiting value is given by Nernst-Hartley relation in terms of the conductance of both the ions whereas limiting value in our work is related by Nernst's expression to the diffusion of thallium ion alone. Hence there is a discrepancy in limiting values obtained by Creeth and Peter ( $D = 1.71 \times 10^{-5} \text{ cm}^2/\text{s}$ ) and us ( $D = 2.1 \times 10^{-5} \text{ cm}^2/\text{s}$ ).

The nature of variation of sodium diffusion coefficients (in sodium chloride aqueous solution) with square root of concentration by different groups of workers is found to be of the same type. But there is a difference in the values of diffusion coefficients at the same temperature and concentration by various groups and methods. Actually the experimental techniques for the determination of tracer diffusion coefficients are not easy with many pitfalls and it is not surprising that the results obtained by Mills (1985), Passiniemi (1983) and other workers vary considerably in the determination of diffusion coefficients for NaCl solutions. Table 1 gives the diffusion coefficient of sodium ion in aqueous sodium chloride solution at different concentrations at 25°C. The only mutual diffusion coefficient measured by us is in Na<sub>2</sub>SO<sub>4</sub> aqueous solution using <sup>204</sup>Tl as the tracer but the variation of  $D$  with concentration shows the same trend as observed in self-diffusion measurements (figure 4).

The diffusion data indicate that in the dilute solutions of MX the fully hydrated  $M$  ion is completely embedded in a sea of water molecules. Since the average distance between the ions in solutions of low concentrations is very large, the hydration as well as the interaction between the hydrated ion and the surrounding solvent water molecules remains essentially the same irrespective of the change in concentrations provided the solutions are dilute. The only effect of increasing the salt concentration in this range is then to increase the interionic attraction due to the long range electrostatic forces. Consequently, the concentration dependence of the diffusion coefficient in this range can be satisfactorily explained by computing the relaxation effect of the Debye-Huckel ion atmosphere. At higher concentrations the picture is



**Figure 4.** Variation of the diffusion coefficient (of Tl ion in aqueous  $\text{Na}_2\text{SO}_4$  solutions) with square root of concentration.

**Table 2.** Thermodynamic transport coefficients in  $\text{mol}^2/\text{ergs cm}$ .

$\text{Tl}_2\text{SO}_4$ soln. in mol l	$L_{11} \times$ $10^{21}$	$L_{12} \times$ $10^{21}$	$L_{22} \times$ $10^{21}$	NaCl.			
				soln. in mol l	$L_{11} \times$ $10^{21}$	$L_{12} \times$ $10^{21}$	$L_{22} \times$ $10^{21}$
0.0002	0.2	0.1	0.2	0.00002	0.01	0.001	0.009
0.0006	0.6	0.4	0.6	0.00009	0.05	0.005	0.7
0.002	2.1	0.9	2.3	0.001	0.64	0.23	1.1
0.006	5.6	2.8	6.2	0.01	6.05	2.01	10.3
0.02	17.0	8.1	18.8	0.10	53.84	15.3	90.3
0.06	44.6	20.1	49.2	0.17	89.53	24.0	149.0
0.15	100.7	35.7	110.2	0.5	230.65	42.0	350.0
0.20	130.3	43.1	147.9	1.0	431.10	91.1	667.0

much more complicated and attempts are being made to utilize Onsager's phenomenological coefficients to explain the diffusion phenomena in this range as done by Chakraborti and Changdar (1984).

The phenomenological coefficients of Onsager are of immense significance for the study of irreversible thermodynamics and for slow processes the range of phenomena covered by these coefficients is very wide. The study of diffusion in liquids is being continued in our laboratory and our experimental results are utilized below for the determination of  $L_{11}$ ,  $L_{12}$  and  $L_{22}$  in table 2. The expressions are

$$L_{11} = \frac{D}{\mu} + \frac{Pt_1^2}{F^2}; \quad L_{22} = \frac{D}{\mu} + \frac{Pt_2^2}{F^2}; \quad L_{12} = \frac{D}{\mu} - \frac{Pt_1t_2}{F^2} \text{ (for 1-1 electrolytes)}$$

$D$  = diffusion coefficient,  $F$  = Faraday,  $t$  = transference number,

$\mu$  = chemical potential and  $P$  = electrical conductance. The relationship between  $D$  (measured) and concentration is given by,  $D \times 10^5 = 1.990 - 0.574\sqrt{C}$  (for  $Tl^{+}$  ion in  $Tl_2SO_4$  soln).  $D \times 10^5 = 1.334 - 0.268\sqrt{C}$  (for  $Na^{+}$  ion in  $NaCl$  solution).

### 3.2 Liquid metals

Mercury and gallium are the two liquid metal systems whose diffusion coefficients were measured by the sliding cell method over a wide range of temperature by Basu *et al* (1980). For measurements with mercury, diffusion cells with diffusion columns of length 2 cm and diameter 0.6 cm were used. Initially the lower cavity was completely filled up with radioactive part having  $^{203}Hg$  as the tracer. Now the amount of non-radioactive mercury required to fill the lower cavity was weighed by means of a very sensitive balance. It was then poured into the hole of the upper slab. Afterwards by the sliding screw arrangement, the solvent column was superposed on the solute column. Recordings were generally taken after one hour of the commencement of diffusion process. The measurements with mercury were made in the temperature range 40–80°C. The diffusion coefficient of gallium was also measured using the above technique. The tracer employed was  $^{72}Ga$  and the temperature range for the measurements was 37°C–80°C. The diffusion data was used to calculate the Stokes-Einstein radius, rate constants and activation energies for these liquid metal systems by Basu *et al* (1976). The Stokes-Einstein radius for mercury comes to around 0.81 Å which is in unexpectedly close agreement with the theoretical prediction. So the theoretical restrictions on the validity of using Stokes-Einstein equations in the case of these two liquid metals can be overruled if we assume that the conduction electrons effectively screen the diffusing ions to provide a kind of hydrodynamic continuum in so far as charge is concerned.

Swalin (1959) considered the self-diffusion in liquid metals from a somewhat different angle. He considered the diffusion resulting from the movement of atoms as a consequence of local density fluctuation. From geometrical considerations he deduced that about four atoms besides the diffusing atom were involved in such a fluctuation. Chakraborti and Changdar (1980) tried to correlate the experimental data in liquid metals with some hard sphere models. Houghton (1964) evolved a simple cubic model for explaining transport phenomena e.g. diffusion, viscosity based on Navier-Stokes equation. Here the central molecule is diffusing and only nearest neighbour interaction is present. On the other hand, Ottar (1935) developed his model from Eyring's jump frequency concept but he assumed that a group of nearest neighbours are diffusing rather than a single molecule. Expressions of diffusion coefficients of Houghton and Ottar are given by

$$D = \frac{kT\rho\lambda^2}{24\eta M} = \frac{RT\rho v^{2/3}}{6\eta M} \text{ (Houghton)}$$

$$D = \frac{RT\rho v^{2/3}}{4\sqrt{2}\eta M} \text{ (Ottar)}$$

where  $\rho$  = density in  $kg/m^3$ ,  $M$  = molar mass in kg,  $\eta$  = viscosity coefficient in poise,



**Table 3.** Measured and calculated values of  $D$  for some liquid metals.

Metal	Temperature in abs. scale	Coeff. of viscosity in Poise	Density in g/c	$D_{th}$ in $m^2 S^{-1}$ from		$D_{exp.} =$ $D \cdot \exp(-e/kt)$ in $m^2 s^{-1}$
				CCM	Ottar's	
Ga	310.0	0.02504	6.0913	1.300	1.380	1.790
	422.0	0.01406	6.0050	2.575	2.700	3.800
	523.0	0.01125	5.9375	3.970	5.420	5.750
Hg	278.2	0.01649	13.5831	1.324	1.405	1.370
	353.0	0.01242	13.4001	2.220	2.360	2.218
	480.0	0.01130	12.485	3.240	3.438	2.958
Pb	613.0	0.0189	10.673	2.345	2.487	2.383
	743.0	0.0144	10.520	3.712	3.938	4.512
			9.590	5.010	5.320	9.778
K	609.9	0.00560	0.669	5.450	5.780	20.79
	773.0	0.00276	0.623	13.700	14.530	32.39
	973.0	0.00185	0.570	24.900	26.410	45.55
Cd	550.0	0.0267	7.379	1.612	1.703	2.40
	650.0	0.0234	7.214	2.234	2.370	3.14
	750.0	0.0186	7.039	3.106	3.295	3.842
Sn	513.0	0.0212	6.597	1.825	1.936	2.410
	673.0	0.0143	6.446	3.520	3.730	4.390
	823.0	0.0113	6.289	5.400	5.730	6.250

$D$  = diffusion coefficient in  $m^2 s^{-1}$  and  $T$  = absolute temperature. Chakraborti and Changdar (1980) utilized the data obtained by sliding cell method and also by other methods for the applicability of these models in the case of liquid metals. This is given in table 3.

#### 4. Conclusions

Comparison of the data obtained by the present method with those obtained by other standard methods (as in the case of metallic mercury, or aqueous thallos sulphate or sodium chloride (solutions)) shows that this integral method of self-diffusion measurement of liquids is potentially accurate and consistent. This method does not have the disadvantages of the diaphragm cell method which results from finding out the constants of the diaphragm. There is also no stirring problem as is encountered in some capillary techniques. The method also gives diffusion coefficient directly and so does not need Stefan-Kawalki tables. Apart from various sources of systematic errors such as temperature fluctuations, mechanical disturbances etc. it is the adjustment of the solute and solvent columns to equal height which presents the principal source of experimental uncertainty. However with the methods adopted by us, the lengths could be adjusted within  $\pm 0.002$  cm without any difficulty. Weak activity of the order of  $50 \mu c$  is generally sufficient for obtaining good counting statistics (Chakraborti (1988)). The method has the further advantage that the zero time correction due to any initial mixing during transference of solvent over the solute is practically eliminated. Finally it can be said that this method is potentially a very simple and accurate one, suitable for most kinds of liquid systems.

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