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Self-diffusion in Liquid Tellurium and Liquid $\text{Te}_{99\%}\text{-Se}_{1\%}$

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Self-diffusion coefficients of Te and Se in pure Te or in $\text{Se}_x\text{-Te}_{1-x}$ ($x=0,01$) alloy, have been measured by using the capillary-reservoir technique. The results are presented by an Arrhenius law, $D = 1,02 \cdot 10^6 \exp. (-35.500/RT)$ for $D_{\text{Te}}^{\text{Te}^*}$ and $D = 0,41 \exp (-9.200/RT)$ for $D_{\text{Se}_x\text{-Te}_{1-x}}^{\text{Se}^*}$ ($x=0,01$).

Results are analysed and compared to solid Tellurium self-diffusion data, Einstein-Stokes-Eyring equation and March-Brown's approximation.

1 INTRODUCTION

Through experiences of neutron scattering (1) X rays (2) or viscosity (3), it has been established that some liquid semiconductors like Te or Se have not the same structure near melting temperature as at higher temperatures.

Likewise measurements of the diffusion coefficient are capable of indicating a structural transition, so we have decided to measure D as a function of temperature in liquid Tellurium, selenium and Te-Se alloys.

2 EXPERIMENTAL METHOD

We have employed the capillary-reservoir method. Other methods, like semi-infinite rods may be advantageous,^{4,5} but are very difficult for liquids like Te or Se. These materials, at liquid state present a great fluidity and run away between the two rods' contact surface. The capillary reservoir method⁶ consists of plunging a capillary of length L , placed vertically in a bath "infinite", which is composed of non activated material (Figure 1). The capillary is filled with a radioactively labelled liquid element. To satisfy the condition of bath "infinite", bath volume must be very great with respect to capillary one.

The capillary extremity is open and this allows the radiotracer to depart from

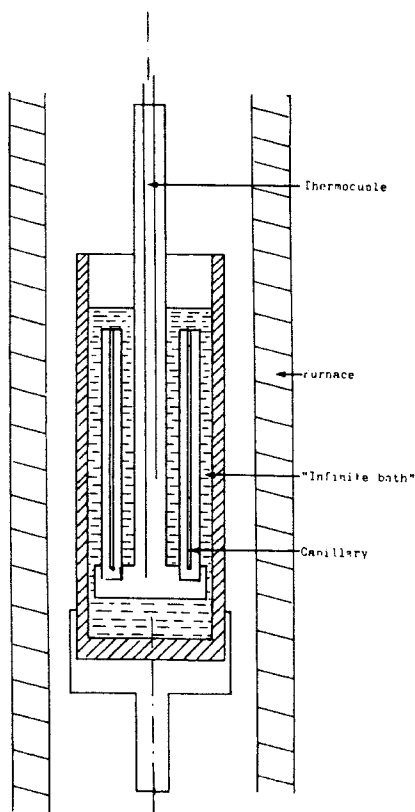


FIGURE 1 Schematic view of "infinite bath" and capillaries.

the capillary into the bath. After a certain time the experiment is stopped and we can measure the diffusion coefficient. Fick's equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

can be solved with the following boundary conditions.

$$\begin{array}{l} t = 0 \qquad 0 < X < L \qquad C = C_0 \\ \left\{ \begin{array}{l} t \neq 0 \qquad C(L,t) = 0 \\ \qquad \qquad \frac{\partial c}{\partial t}(0,t) = 0 \end{array} \right. \end{array}$$

The solution is the well-known expression

$$\frac{\bar{C} - C_0}{C_0 - C_i} = \frac{8}{\pi^2} \sum \frac{1}{(2n+1)^2} \exp \left[- \frac{(2n+1)^2 Dt}{4L^2} \right]$$

\bar{c} = mean average concentration; c_i = initial bath concentration.

c_0 = initial capillary concentration; t = diffusion time.

D = diffusion coefficient; L = capillary length.

We have employed graphite capillaries of 5-7 cms. length and 1 mm. diameter.

The reasons of graphite choice are:

- a) Graphite is chemically inert with respect to Te and Se.
- b) its thermal conductivity is near to these elements, so thermal equilibrium is quickly attained.
- c) its porosity avoids bubble gas formation.

The filling of capillaries was performed by fixing them in the bottom of a graphite crucible (Figure 2) which contains a "mixture" of non-activated Te (99,9%) and activated Te^{127}_{52} (0.1%). The "mixture" was heated up to 550°C.

Pressurised argon gas was admitted into the furnace to aid the operation. Before admittance of argon, capillary tubes were de-gassed under 10^{-5} mm of pressure (Figure 2) Radioactive isotope was Te^{127}_{52} with a half-period of 109 days. After

filling, capillaries and bath were placed separately in the furnace. When the desired temperature is attained, the capillary is sunk in the bath. All the experimental operation was carried out under argon pressure (4 kg.), because of the liquid Tellurium high vapour tension. To avoid convective phenomena, a small positive temperature gradient (0,1°C/cm.) was created. Temperature fluctuations ($\pm 0,5^\circ C$) were recorded on a M.E.C.I. type recorder potentiometer.

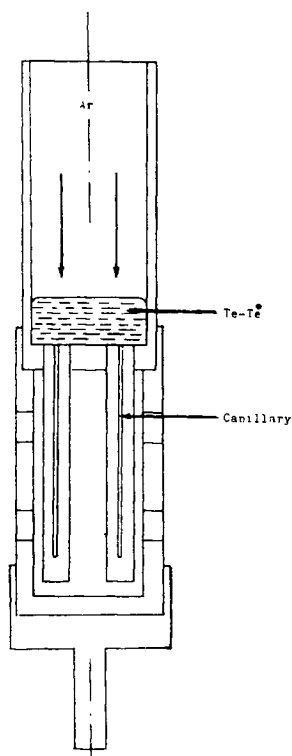


FIGURE 2 Diagram shows the procedure for the filling of the capillaries.

Time diffusion run was adjusted to keep boundary conditions; in order to verify them, control was made with a witness. By γ radiation analysis we can determine average concentration and eventually profile concentration.

3. EXPERIMENTAL RESULTS

Twelve determinations of Te self-diffusion coefficient were carried out, as a function of temperature. Results are shown in Table I. The temperature interval was between 733 K and 814 K.

The relative error can be evaluated to 10% and it arises principally from the fact that boundary conditions at the free extremity of the capillary had not been thoroughly respected. We can neglect other sources of error like concentration, non-homogeneties, temperature fluctuations and analysis measurement dispersion.

TABLE I

Experimental self-diffusion coefficients of liquid Tellurium at different temperatures, capillary lengths and diffusion times

D. 10 ⁵ (cm ² - sec ⁻¹)	Temperature (K)	L (cms)	t (sec.)
2.5	735	6.89	72,000
2.6	741	5.85	83,700
3.0	738	7.0	36,000
4.0	743	7.0	66,300
3.6	745	7.0	36,000
4.8	751	5.0	32,400
4.5	754	5.0	32,400
4.9	769	7.0	86,400
4.9	773	7.0	36,000
5.1	783	7.0	36,000
4.9	789	5.0	32,400
4.4	814	7.0	50,400

In Figure 3 the ln D variation versus 1/T is represented. The Arrhenius plot clearly shows two different domains.

a) Interval between melting temperature (T_f) and T_f + 30 K; in this interval adjustment by least square method, of Arrhenius law $D = D_0 \exp (-Q/RT)$ gives the activation energy and the pre-exponential term.

Obviously these two terms are abnormally high for metal or semi-metal liquids.⁷

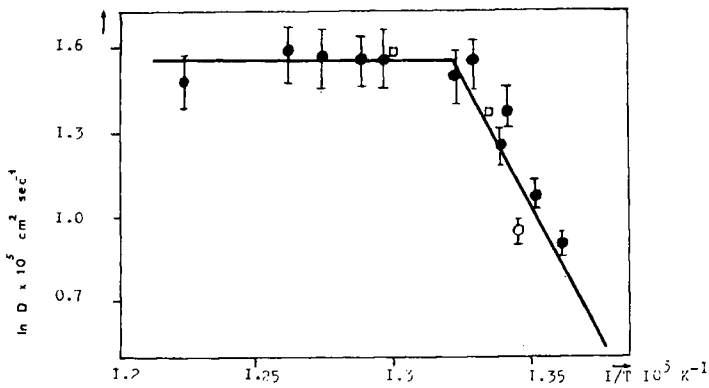


FIGURE 3

● Ln D vs 1/T plot for the self-diffusion coefficient of liquid Tellurium.

○ Neutron inelastic scattering value⁸.

□ $D_{Te_{1-x}Se_x}$ (x = 0.01)

b) interval between $T_f + 30\text{ K} - 814\text{ K}$:

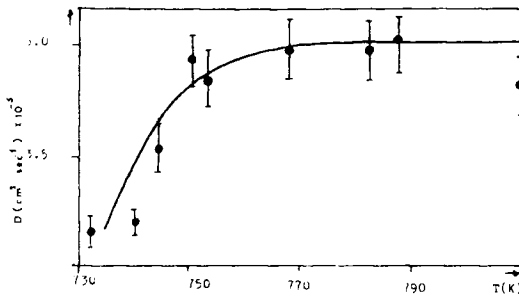
at higher temperatures, T_e self-diffusion coefficient changes very slowly and because of experimental point dispersion it is not possible to evaluate Q and D_0 accurately.

However these two parameters are certainly far from those of liquid metals. In Figure 4, a comparison is made between viscosity and self-diffusion coefficients, as a function of temperature; the similarity in behaviour being strong.

Similarly the reservoir-capillary method was employed to measure Se and $\text{Te}_{1-x} - \text{Se}_x$ diffusion coefficients. In the case of liquid selenium several difficulties have appeared; the principal one arose from the great volume variation when selenium passes from solid to liquid state (16,8%) (see ref. 3). So, when the diffusion experiment is finished an important capillary portion is empty, and it is impossible to obtain accurate results.

However it was easy to verify that selenium self-diffusion coefficient is one order of magnitude smaller than liquid metal coefficient.

This is not a surprising result because, as we can see, viscosity³ and neutron inelastic scattering measurements⁸ indicate that a long "chain" structure conservation must be expected in liquid Se .



Temperature dependence of the self-diffusion coefficient of the liquid Tellurium.

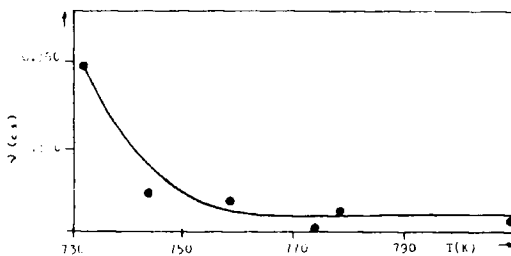


FIGURE 4 Temperature dependence of the viscosity coefficient of liquid Tellurium.

Finally the self-diffusion coefficient values for $D_{\text{Te}_{1-x}\text{Se}_x}^{\text{Se}^*}$ and $D_{\text{Se}}^{\text{Se}^*}$ are indicated in Tables II and III.

For $D_{\text{Te}_{1-x}\text{Se}_x}^{\text{Se}^*}$ Arrhenius law parameters are $D_0 = 0,41 \text{ cm}^2 \text{ - sec}^{-1}$ and $Q = 8,2 \text{ K-cal-mole}^{-1}$.

In opposition to pure Tellurium, atomic mobility of selenium in liquid dilute alloys is large.

4. DISCUSSION

As opposed to some liquid metals (like Na), the materials which we have studied, have no central symmetry. So, this prevents us from applying Kirkwood-Rice's theory⁹ which links diffusion coefficient with pair correlation function, $g(r)$, and interatomic potential, $V(r)$.

Nevertheless, even a less deep analysis can help us to understand the structure of these materials.

TABLE II

Experimental diffusion coefficients for the diffusion of Se^* in $\text{Te}_{1-x}\text{Se}_x$ ($x = 0,02$) at different temperatures capillaries lengths and diffusion times.

$D_{\text{Te}_{1-x}\text{Se}_x}^{\text{Se}^*} \cdot 10^4 \text{ (cm}^2 \text{ - Sec}^{-1}\text{)}$	Temperature(K)	L (cms)	t (sec)
1.5=	742	4.0	9,600
1.2	751	4.0	9,600
1.6	758	7.0	9,600
1.9	764	4.0	10,800
1.8	766	7.0	9,600
2.3	781	7.0	22,500

TABLE III

Experimental self-diffusion coefficients of liquid selenium at different temperatures, capillary lengths and diffusion times.

$D \cdot 10^5 \text{ (cm}^2 \text{ - sec}^{-1}\text{)}$	Temperature(K)	L (cm)	t (sec)
0.76	528	6.9	82,800
0.45	568	7.0	147.600

4.1. Liquid tellurium

As has already been pointed out, a remarkable slope change in the neighborhood of $T_f + 30$ K was observed.

As a matter of fact, although D_0 and Q values are large, absolute values of T_e self-diffusion coefficient values are, in order of magnitude, similar to most of liquid metals.

First, we shall compare them to those of solid Te. Ghoshtanghore¹⁰ has measured self-diffusion coefficient of Te single-crystals between 573 K and 673 K. The reported activation energy and pre-exponential terms are.

$$\begin{aligned}
 Q_{\parallel} [0001] &= 40 \text{ k-cal-mol}^{-1} \\
 Q_{\perp} [0001] &= 46 \text{ k-cal-mol}^{-1} \\
 D_{o\parallel} [0001] &= 1,03 \times 10^2 \text{ cm}^2\text{-sec}^{-1} \\
 D_{o\perp} [0001] &= 3,91 \times 10^4 \text{ cm}^2\text{-sec}^{-1}
 \end{aligned}$$

It can be noted that $Q_{\text{solid}} \sim Q_{\text{liquid}}$: if we assume that high activation energy means high peak barrier value, it is natural to infer that strong covalent bonds persist in liquid state between T_f and $T_f + 30$ K.

As regards D_0 , Goshtanghore attempted to explain its elevated value by the following fact:

according to classic hole diffusion theory

$$D_0 = d^2 \left(\frac{k_8}{h} \right) \exp (\Delta S/R)$$

Only a high value of $\Delta S/R$ accounts for D_0 high estimation because other parameters (d , θ), in Te case are not fundamentally different from other metals and semi-conductors.

$$\left| \frac{\Delta S}{R} \right|_{\parallel [0001]} = 6,06 \quad \left| \frac{\Delta S}{R} \right|_{\perp [0001]} = 10,65$$

This fact is related to a high degree of disorder; we can suppose that strong vibrations about equilibrium positions are the cause of this disorder. When melting is produced, this highly disordered state is increased, not only by vibrational but also by translational motions.

$$\left| \frac{\Delta S}{R} \right|_{\text{Liquid}} \sim 19,6$$

Glazov³ has presented a very pictorial description of these facts. Following him, we can assume that liquid Te between T_f and $T_f + 30$ K is composed of

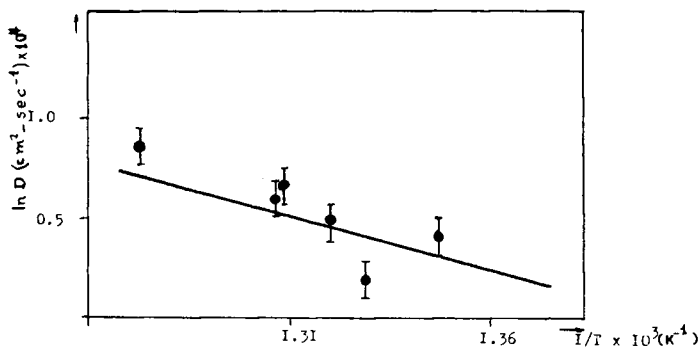


FIGURE 5 $\ln D$ vs $1/T$ plot for the diffusion of Se in $\text{Te}_{1-x}-\text{Se}_x$ ($x = 0.01$)

residual elements of solid structure (atomic “chains”) and non-bonded atoms. If we accept that “chain velocity” is very small, measured self-diffusion coefficient is due almost only to “free” atomic mobility.

When temperature increases, the number of non-bonded atoms also increases, due to “chain” dissociation and consecutively D values change very quickly. Although in all this description, strong covalent bond hypothesis is not explained, it is implicitly assumed by the fact of “chain structure” supposition. Finally, at higher temperatures, “chain structure” has disappeared, so diffusive motion is only due to atomic Te movements and the self-diffusion coefficient changes very slightly. J. Friedel and G. Cabane¹¹ taking into account elastic neutron scattering measurements¹ suggest the existence of a structural transition close to $T_f + 30 \text{ K}$; below this temperature, liquid Te has a $\text{Te}_2 + 4$ structure: first two neighbours and second four neighbours; just above $T_f + 30 \text{ K}$ Te evolves to a $\text{Te}_3 + 3$ structure. Both descriptions (Glazov’s and Cabane-Friedel’s) are similar if one admits that $\text{Te}_2 + 4$ bonding energy is stronger than $\text{Te}_3 + 3$. It is also interesting to compare the experimental self-diffusion coefficient with the values calculated from Einstein–Stokes–Eyring equation

$$D = kT/z \left(\frac{V}{N} \right)^{1/3} \eta$$

$z =$ number of first neighbours: $\frac{V^{1/3}}{N} \sim 2 r$ (mean average distance to first neighbours); $\eta =$ viscosity coefficient.

We have put $z = 6$; of course it is a rough approximation but, because of the lack of symmetry of liquid Te, there is no sense in trying to give an “exact” value of z . Choosing the interatomic distance $\left(\frac{V}{N} \right)^{1/3}$ is equivalent here, to taking a mean value between the first neighbours (2 or 3) and second neighbours (3 or 4). Figure 6 shows theoretical and experimental curves.

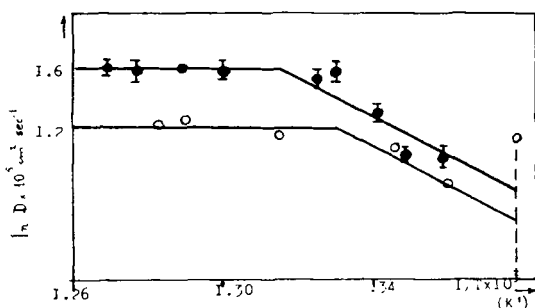


FIGURE 6 Comparison between experimental and theoretical values.
 ● Experimental values
 ○ Theoretical values according with Einstein-Stokes-Eyring's theory.

It is very interesting to see that in spite of a questionable choice of parameter values, both curves are not so different in order of magnitude and behaviour. A different way of analysing self-diffusion coefficient results, arises from the use of self-correlation velocity function, $z(\xi)$ or its Fourier transform $\tilde{z}(\omega)$. From the well-known relations $\tilde{z}(0) = D/\pi$, $\int_{-\infty}^{\infty} \tilde{z}(\omega) c \omega = kT/\eta$ R. C. Brown and N. H. March¹² have proposed an extremely simple relation, which links D with characteristic material parameters.

$$D \sim \frac{kT_f}{\omega_D M}$$

where T_f = melting temperature
 ω_D = Debye-cut-off frequency
 M = atomic mass

We have extrapolated our results to 725 K (T_f) and obtained the following results.

$D_{\text{exp}} \cdot 10^5$	Temperature (K)	Debye (K)
1,8	725	190

If we compare with θ_D of solid Te (141 K) it can be seen that March-Brown's approximation is qualitatively correct.

Unfortunately, so far, no experimental measurement of $\tilde{z}(\omega)$ of Te have been performed.

When we reach $T_f + 30$ K, liquid Tellurium is mainly composed of $\text{Te}_3 + 3$. At this temperature the self-diffusion value is $4,5 \cdot 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$ approximately and hence from the March-Brown approximation $\theta \sim 79$ K.

At higher temperatures the liquid Tellurium interatomic bonds became more weak,^{11,13} consequently it is not unreasonable to think that the vibration values decrease. Using the March-Brown approximation we can represent the $\tilde{z}(\omega)$ variation as shown in Figure 7.

Of course this is only a crudely schematic representation since the real shape, of the $\tilde{z}(\omega)$ function would be much more complicated.

This variation in the vibration frequencies could explain (qualitatively) the abnormally high value of the fusion entropy.

$$S_s - S_L = \Delta S_F = 5,8 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

Because experimental determinations of ΔS_F have not been performed near T_f , we suppose this value to be related to the $\text{Te}_2 + 4 \rightarrow \text{Te}_3 + 3$ transition.

If we use Einstein's expression¹³

$$\Delta S_F = 3 R \ln (\theta_2 + 4 / \theta_3 + 3) \sim 5,2 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

It must be remarked that in neutron inelastic scattering experiments⁸ performed at 470°C the solid state spectral peaks are not present.

Finally we will analyse the behaviour of impurities in Te-Se liquid alloys. Three conclusions can be inferred from experimental results: -

- atomic mobility of liquid Se is very much smaller than liquid Te mobility. This fact can be related to the cycle-chain structure of liquid Se. It can be considered that liquid Se interatomic bonds are even stronger than those of $\text{Te}_2 + 4$.

- Very dilute Se (1 o/o in atomic fraction), in liquid Te, diffuses faster than the solvent itself.

$$D_{\text{Se}_x}^{\text{Te}^*} - \text{Te}_{1-x} \text{ is practically the same as } D_{\text{Te}}^{\text{Te}^*}$$

- Se-Te bound energies are weaker than Te-Te.

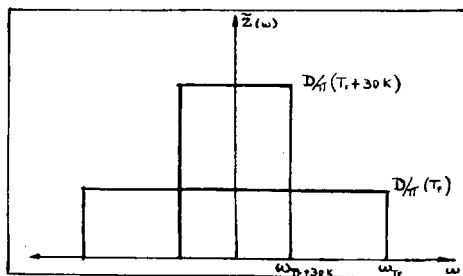


FIGURE 7 March-Brown's approximation.

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