zone), its rate of motion is approximately 2.9 cm/year.

In conclusion, our data suggest that Madagascar could have moved south from Somalia, beginning in the early to middle Cenozoic, but not east from Mozambique. If it is possible to drill to basement with the forthcoming deep-sea drilling program in the Mozambique Channel, one can see if the basement predates the Cenozoic.

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Motions of Molecules in Liquids: Viscosity and Diffusivity

Abstract. *The fluidity of a simple liquid is proportional to its degree of expansion over the volume,* V_0, *at which its molecules are so crowded as to inhibit self-diffusion and viscous (as distinguished from plastic) flow. The equation of proportionality is* $1/\eta = B[(V - V_0)/V_0]$ *where* η *is the viscosity and* V *is the molal volume. Values of* B *are the same for normal paraffins from* C_3H_8 *to* C_7H_{16} *and then decrease progressively as the paraffin lengths increase. Values for other liquids,* C_6H_6, CCl_4, P_4, CS_2, $CHCl_3$, *and Hg, appear to vary with repulsive forces. Liquids can be moderately fluid when expanded by less than 10 percent; this shows the unreality of some theoretical treatments of the liquid state. Diffusivity begins from the temperature at which* V *equals* V_0 *and can be correlated for temperature dependence, and for solute-solvent interrelations.*

Bird, Stewart, and Lightfoot had this to say in chapter 16 of their extraordinarily fine book on *Transport Phenomena* about the present state of theory of diffusion in liquids (*1*):

> If the reader has by now concluded that little is known about the prediction of dense gas and liquid diffusivities, he is correct. There is an urgent need for experimental measurements, both for their own value and for the development of future theories.

I see two reasons for this lack of general theory. One, measurements have not been designed to obtain answers to questions of general significance. Although, for example, diffusion is an example of entropy increasing toward the maximum permissible under the conditions, very few of the vast number of measurements of diffusivity (*2*) were made at more than one temperature. Also, statistical mechanicians have treated transport theory as essentially a problem in mathematics. In papers and symposia dealing with the theory of the liquid state, few of the authors have sought validation by experimental facts. The volume recording the proceedings of the International Symposium on Transport Processes in Statistical Mechanics (*3*), held in Brussels in 1956, is typical. In the first half of the book there is only one paper containing any reference to experiment. Otto Redlich has said that science, unlike mathematics, is not autonomous; its concepts must be referred to nature for validation. Theorists do not always do that.

I approach the problem of diffusion by way of viscosity, the much simpler phenomenon. Viscosity of liquids has been treated copiously in engineering and scientific literature, but nearly all that I have read seems unrealistic in one respect or another, such as the assumption of quasi-lattice structure that ignores clear evidence to the contrary, or that temperature dependence is exponential, or that there is an energy of activation, a notion that disregards the basic distinction between liquid and plastic flow.

Batschinski (*4*), in 1913, published an important paper that has been virtually ignored by authors on transport phenomena; I found it only recently, almost by accident. Batschinski reasoned that viscosity is not a direct function of temperature but of the difference between the specific volume of the liquid, v, and a certain constant, ω, similar to the van der Waals b. He wrote his relation $\eta = c/(v - \omega)$, where c is another constant. He plotted v against fluidity, $1/\eta$, for 87 liquids, obtaining straight lines for those that are not associated. The values he thus obtained for ω fell between specific volumes of liquid and solid and were nearly the same fraction of critical volumes. His effort to evaluate c as an additive of atomic parameters was not successful.

I propose a modification of Batschinski's formulation as follows. Fluidity depends on the the ratio of free volume, $V - V_0$, to intrinsic volume, V_0, the molal volume at which fluidity is zero. I prefer molal volume to specific volume for conceptual reasoning. By analogy with Batschinski's procedure I write

$$\eta = C/(V - V_0) \qquad (1)$$

I plot measured values of fluidity, $1/\eta$, against molal volume, V. All the simple liquids I have examined, added to the scores Batschinski investigated, give straight lines that yield values of V_0 at the intercept, where $1/\eta = 0$. The slopes of the lines give values of C. Typical cases are illustrated in Figs. 1 and 2 showing the variation of viscosity with temperature of C_3H_8, C_6H_6, and CCl_4. Figure 3 is a plot of fluidity against V for C_6H_6 and CCl_4. Values of V_0 and C are given in Table 1 for these and other liquids, determined in this way. Batschinski, by multiplying his values of specific volume at zero fluidity by molecular weight, obtained values of V_0 which quite agree with mine for the same liquids. He discovered that the ratios of his values of V_0

Table 1. Parameters of Eqs. 1 and 2.

Molecule	V_0 (cm³/mole)	C	B
C_3H_8	61	3.27	18.6
C_5H_{12}	92	5.10	18.5
C_6H_{14}	111	6.18	18.0
C_7H_{16}	130	6.88	18.8
C_8H_{18}	147	8.58	17.1
C_9H_{20}	165	10.0	16.5
$C_{10}H_{22}$	183	12.2	15.2
$C_{12}H_{26}$	217	15.4	14.1
C_6H_6	82.0	4.44	18.5
p-$C_6H_4(CH_3)_2$	114.5	6.24	18.4
CCl_4	88.3	5.06	17.4
P_4	68.6	4.22	16.3
CS_2	50.5	3.59	14.0
$CHCl_3$	70	5.00	14.0
Hg	14.10	1.12	12.6

to the critical volumes for nonassociated liquids vary but little from 0.31. In the cases of CCl_4, CS_2, and P_4, which freeze to solids that retain rotational energy, their solid molal volumes, V_s, are 87.9, 49.0, and 67.7 cm³, respectively, close to their values from fluidity, given in Table 1. The values of viscosity for most of these liquids are from the handbook (*5*). The data for P_4 are from Powell, Gilman, and Hildebrand (*6*); those for xylene are from Smith and Hildebrand (*7*).

It is obvious from the small scatter of the points from the lines in Fig. 3, which yielded the parameters V_0 and C, that the viscosities of the liquids could be recalculated accurately by Eq. 1 with the parameters in Table 1.

I have modified Eq. 1 so as to recognize the fact that fluidity must depend upon relative expansion, $(V - V_0)/V_0$:

$$\frac{1}{\eta} = B\frac{V - V_0}{V_0} \qquad (2)$$

The parameter $B = V_0/C$. Values of the three parameters, V_0, C, and B, are listed in Table 1. It is striking that the values of B for such different liquids as C_3H_8 and C_7H_{16} are the same within the inaccuracies of the data. This may be explained by the orientation of molecules with their long axes in the direction of flow. The progressive decrease in B among the higher members may be the result of increasing flexibility. I can report that the values of V_0 for the normal paraffins are accurately linear with molecular weight, a fact that can serve in interpolating missing values.

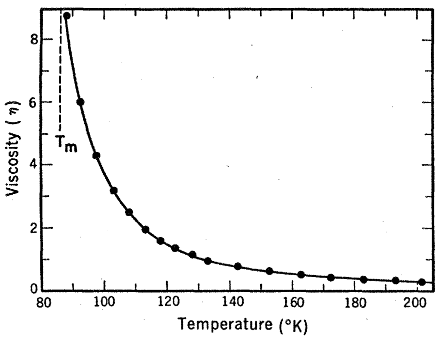
It is instructive to consider the magnitude of expansion as revealed by the values of fluidity. Table 2 gives values at 20° and 40°C calculated by Eq. 2 from values of $1/B\eta$. We see that at 20°C CCl_4 has to be only 6 percent expanded over its intrinsic volume in order to have the rather low viscosity of 0.97 cp. Again, C_6H_6 has a viscosity of 0.65 cp when only 8 percent expanded. Such small free volumes correspond to mean free paths of only a few percent of molecular diameters. These figures are in harmony with the calculations for hard sphere fluids of Alder and Einwohner (*8*) who reported that the probability of a mean free path as long as a molecular diameter in a liquid for which $V/V_0 = 1.6$ is 4×10^{-8}.

The fact that a liquid can be so fluid although expanded so little over its intrinsic volume is evidence of the unreality of some of the concepts that have been used by writers on transport theory, concepts such as "trajectories" between separable "collisions," some of which are "hard" and others "soft," and "cages" in which a molecule is "oscillating" with a definite frequency while awaiting an access of "activation energy" sufficient to enable it to break through a "barrier" into a "hole" awaiting it at a distance of exactly one diameter.

Table 2. Values of relative free volume, $(V - V_0)/V_0$, at 20° and 40°C, calculated from $1/\eta B$.

Liquid	T (°C)	η (centipoise)	$\frac{V - V_0}{V_0}$
CCl_4	20	0.97	0.059
	40	.74	.078
C_6H_6	20	.650	.080
	40	.492	.112
CS_2	20	.366	.184
	40	.349	.194

Applying to diffusivity the results of our study of fluidity, we can expect, first, that both begin at the same tem-



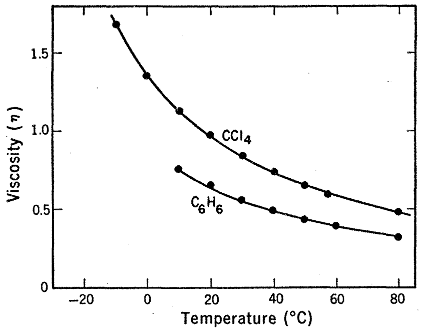


Fig. 1 (left). Variation of viscosity (η) of C_3H_8 with temperature; viscosity is in centipoise. Fig. 2 (right). Variation of viscosity (η) of C_6H_6 and CCl_4 with temperature.

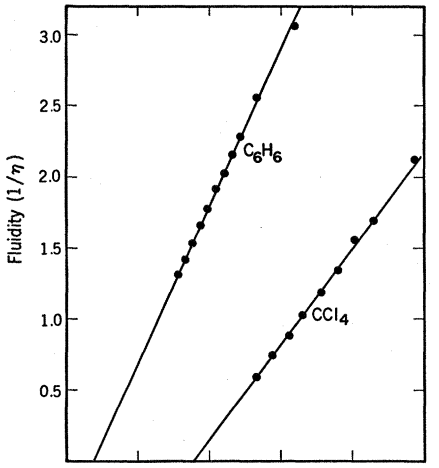


Fig. 3 (left). Variation of fluidity $1/\eta$ with molal volume of C_6H_6 and CCl_4. Fig. 4 (right). Variation of diffusivity (D) (in cm²/sec) with temperature for C_6H_6 and CCl_4 (○), CCl_4 in C_6H_6 (●), and I_2 in CCl_4 (+).

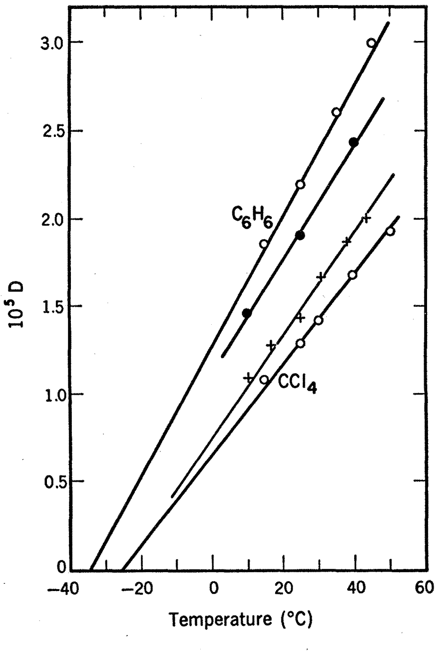


Table 3. Observed diffusivity of gases in CCl_4 at 25°C compared with values calculated from the self-diffusion coefficient of CCl_4 and ratios of molecular cross sections.

Quantity	CCl_4	CF_4	CH_4	N_2	Ar
V_c (cm^3/mole)	276	145	98.6	90.0	74.5
$V_c^{2/3}$	42.5	27.5	21.3	20.1	17.7
$10^5 D$(obs) (cm^2/sec)	1.41	2.04	2.78	3.42	3.63
$10^5 D$(calc) (cm^2/sec)	——	2.18	2.81	2.97	3.38

perature and molal volume as linear functions of $(V - V_0)/V_0$. Experimental evidence in the case of diffusivity is small in volume but good in substance and quality. I begin with recent determinations of the self-diffusion coefficients of C_6H_6 and CCl_4 between 15° and 50°C by Collings and Mills (*9*) (Fig. 4). The lines are quite straight and extrapolate to −35° and −25°C, respectively. C_6H_6 freezes to a laminar solid at 6°C, but CCl_4 freezes to a solid with rotating molecules and a molal volume of 87.9 cm^3 that is close to 88.3 cm^3, the value derived from viscosity. V_0 for C_6H_6 was found to be 82.0 cm^3 from viscosity; this is its critical molal volume, 256 cm^3, multiplied by 0.32, the factor that holds for a number of liquids.

Watts, Alder, and Hildebrand (*10*) had earlier measured the self-diffusion of CCl_4, obtaining values about 0.1 higher but parallel to those of Collings and Mills.

The greater slope of the line for C_6H_6 in Fig. 4 may be explained without a complete analysis of the problem. Molecules of C_6H_6 in free space move much faster than those of CCl_4. From the equation $1/2\ mv^2 = 3/2\ kT$, where m denotes molecular mass, v is the velocity in free space, and k is the Boltzmann constant, it follows that at the same temperature $v_B/v_A = (m_A/m_B)^{1/2}$; therefore, letting m_B stand for benzene and m_A for CCl_4, since $(m_A/m_B)^{1/2} = (154/78)^{1/2}$, $v_B/v_A = 1.41$. The ratio of the slopes of the lines in Fig. 4 is 1.63.

Self-diffusion is actually a misnomer; it is determined by introducing a small concentration of molecules tagged so that they can be recognized, but in a way that does not measurably alter their diffusivity. Under this restriction they form an ideal solution; there is no enthalpy of dilution and the free energy of dilution is T times the entropy of dilution. This kind of free energy is purely statistical; it is not a vector force acting upon individual molecules, impelling them "downstream" against a resistance.

Passing on next to the diffusivity of a dilute solute, let us consider the diffusivity of iodine in CCl_4, determined in 1953 by Haycock, Alder, and Hildebrand (*11*). Their points have been added to Fig. 4. Because the solvent controls the motions of isolated solute molecules, the straight line through the points extrapolates to the same temperature as the line for the solvent. It is moderately displaced upward because the cross section of iodine molecules is less than that of CCl_4.

The line for dilute CCl_4 in C_6H_6 lies below the line for the solvent by almost exactly the ratio of their slopes, 0.87, compared with the ratio of the ⅔ power of their partial molal volumes, 0.89.

That the line of D plotted against T for a solute starts at the temperature of zero fluidity of the solvent is strikingly illustrated by the data obtained by Ross and Hildebrand (*12*) for diffusion of gases in CCl_4. They found that the ratios of diffusivity at 25°C to those at 0°C were 1.41 for CH_4 and CF_4, and 1.48 for N_2. The ratio of $(V - V_0)/V_0$ for CCl_4 at 25°C to that at 0°C is 1.47. So much for the temperature coefficient of solute diffusivity.

They found also that the diffusion constants of various solutes and that of isotopic CCl_4 are inversely proportional to their molecular cross sections. Using "best" values of molecular diameters, σ, they obtained the following relative values of $D\sigma^2$ for solutes and solvent: 47 for CCl_4, 44 for CF_4, 43 for CH_4, and 46 for N_2. The product became 66 for D_2 and 86 for H_2 from the entrance of a quantum effect. This increases linearly with the square of de Boer's quantum mechanical parameter—excess of zero point energy over classical translational energy—to include ^{4}He (*13*) and ^{3}He (*14*). The diffusivity of the nonquantum gases in CCl_4 can be calculated with remarkable approximation from the cross section and the self-diffusivity of CCl_4. Relative values of molecular cross sections in fluids can be obtained from critical volumes (V_c). Table 3 gives values of V_c and $V_c^{2/3}$ for CCl_4 and four gases. The diffusivity of these gases in CCl_4 at 25°C has been calculated from the coefficient of self-diffusion of CCl_4, which I take as 1.41×10^{-5} (*10*) multiplied by the ratio of $V_c^{2/3}$ for CCl_4 to $V_c^{2/3}$ for the gas. This procedure yields the values of $10^5 D$ (calc), which can be compared with the experimental values $10^5 D$ (obs), in the table. In view of the difficulty of making precise determinations of diffusivity and the long extrapolations involved, the agreement is remarkable.

Attempts to calculate absolute values of diffusivity have been made by starting from Stokes' law for a particle settling under the pull of gravity, and extrapolating over the long path to a molecule participating with its neighbors in aimless thermal motions that are never as long as the molecular diameter. Individual molecules are not impelled by a vector force that can serve to measure a "coefficient of friction." Any such coefficient is fictitious.

If molecules were hard spheres, instead of electron clouds with imbedded nuclei, and were sufficiently far apart to justify speaking of binary collisions with linear free paths between them, the probable distance they could be expected to wander from their initial positions could be computed by the formula for a "random walk." But polyatomic molecules that move less than 10 percent of their diameter require a more sophisticated mathematical formulation. They are in a continual state of soft, slow collision, with constant exchange between translational and internal energy. The random walk in this case is a slow, tipsy reel, without sudden changes of direction. The mathematical problem involved is similar to that of calculating the probable distance between the two ends of a string, say 100 feet long, after gathering it rapidly into a tight ball. Since I am interested only in getting transport theory on a course upon which it can be expected to progress toward a solution, I make no effort, at least at present, to try to solve the problem of the ball of string. To start something that tempts others to carry on can be more rewarding than something one can finish alone.

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Intercalation Complexes of Lewis Bases and Layered Sulfides: A Large Class of New Superconductors

Abstract. *Exploration of the generality of the recently discovered reaction whereby certain organic molecules can be inserted between the metallic layers of the superconductors tantalum disulfide and niobium disulfide revealed that a large variety of organic and inorganic molecules can penetrate between the crystalline layers of a number of transition metal dichalcogenides and that the resulting complexes are superconducting if the layered chalcogenide from which they are formed is superconducting. The critical temperatures of the 50 new superconductors we report depend on the nature of the intercalate but are insensitive to a separation of the superconducting planes of up to 57 angstroms.*

The compound $TaS_2(C_5H_5N)_{1/2}$ is a crystalline superconductor (critical temperature $T_c = 3.5°K$) in which metallic TaS_2 planes 6 Å thick are separated by layers of pyridine 6 Å thick (*1*). This structure was originally derived from x-ray diffraction data and has now been confirmed and extended by Fernández-Morán *et al.*, using electron microscopic imaging techniques [see (*2*)]. The pyridine complex and similar complexes that we report on here are probably the most anisotropic superconductors known. They are also the only crystalline metallic systems that are in large part organic, and, consequently, they offer us a unique opportunity to examine a number of speculations regarding interactions between conduction electrons and molecular electrons which might result in new kinds of superconductivity (*3*). As one should expect from their remarkable structure, such superconductors possess a number of unique superconducting properties. For instance, the depression of the critical temperature with magnetic field (dT_c/dH) is less in these materials than in any other known superconductor. Fields of 60 kilogauss applied parallel to the layer depress the critical temperature by only half a degree (*4*). Another unique feature of these superconductors is the apparent formation of evanescent Cooper pairs at temperatures in excess of ten times the critical temperature. A small diamagnetic contribution to the susceptibility is observed even above 50°K and grows slowly in a Curie-like manner as the temperature is lowered (*5*). It appears that constraining the electrons to motion along the TaS_2 planes in these crystals has enhanced the stability of evanescent Cooper pairs with the result that they are observed at higher temperatures than ever before. These results, the novelty of the materials, and the hope that some of the speculations regarding higher critical temperatures in such systems might be well founded have encouraged us to try to define the limits and nature of this new class of materials by examining TaS_2 and other layered chalcogenides and intercalates other than pyridine. In particular, we wished to determine whether the superconducting critical temperature could be affected in an understandable or dramatic way by varying the intercalate and whether the superconducting properties would be altered by increasing the distance between superconducting planes.

There are about 40 binary layered chalcogenides (*6*). We have prepared intercalation complexes of many of them. Some, however, are considerably more difficult to prepare and to characterize than others. Here we report only on our studies of the intercalation complexes of the group IV b and V b disulfides, especially TiS_2, NbS_2, and TaS_2. Titanium disulfide is a degenerate semiconductor, whereas NbS_2 and TaS_2 are superconducting metals. All three compounds are composed of parallel layers in which a plane of metal atoms is sandwiched between two planes of sulfur atoms. The atoms in each plane are arranged in a hexagonal array. Both NbS_2 and TaS_2 are polymorphic. Here we shall be concerned only with the 2H-phase of each. In the 2H-phase, the sulfur atoms in the two planes within the sandwich superpose and the metal atoms are found at the center of half the trigonal prisms formed by the sulfur. On the basis of the notation for the closest packing of spheres, the structure of 2H-TaS_2 and 2H-NbS_2 is *AbACbC*, where the capital letters refer to the sulfur atoms and the lowercase letters refer to the metal atoms. In TiS_2 the sulfur planes do not superpose. The structure is *AbCAbC*, and the titanium is in an octahedral environment. Bonding within the layer is strong and primarily covalent, whereas that between layers is mainly van der

Table 1. Chemical analysis of some complexes.

Complex	Percentage (by weight) found						Percentage (by weight) calculated					
	Nb/Ta	S	C	H	N	P	Nb/Ta	S	C	H	N	P
$NbS_2(\text{aniline})_{1.0}$	36.8	25.4	28.8	3.10	5.85		37.1	25.6	28.8	2.82	5.60	
$NbS_2(\text{tributylphosphine})_{1/8}$	51.0	35.0	9.86	1.94		2.03	51.0	35.2	9.88	1.87		2.11
$TaS_2(\text{TMPD})_{1/4}$*	63.6	22.6	10.3	1.40	2.41		63.3	22.4	10.5	1.39	2.44	
$TaS_2(\text{tributylphosphine})_{1/8}$	67.3	23.9	6.50	1.31		2.08	66.9	23.7	6.66	1.26		1.43

* TMPD = tetramethyl-*p*-phenylenediamine.