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The Effect of Pressure on Diffusion in CS₂ Organic Mixtures*

R. C. KOELLER AND H. G. DRICKAMER

Department of Chemistry, University of Illinois, Urbana, Illinois

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Diffusion coefficients are presented as a function of pressure to 10 000 atmospheres for the following systems:

- 50 mol percent *n*-heptane—50 percent CS₂ 0°–20°–40°;
- 50 mol percent 2,4 dimethylpentane—50 percent CS₂ 20°–40°;
- 50 mol percent toluene—50 percent CS₂ 20°–40°;
- 50 mol percent methylcyclohexane—50 percent CS₂ 0°–20°–40°;
- 50 mol percent *n*-octane—50 percent CS₂ 20°C;
- 50 percent chlorobenzene—50 percent CS₂ 20°–40°;
- 80 percent chlorobenzene—20 percent CS₂ 40°;
- 50 percent *n*-butanol—50 percent CS₂ 20°–40°;
- 50 percent iso-butanol—50 percent CS₂ 20°–40°;

using S³⁵ tagged CS₂.

The results are interpreted in terms of the activation volume, enthalpy, and entropy, and conclusions are drawn concerning the effect of pressure on the structure of the liquids.

IN a previous paper¹ a method was described for measuring diffusion coefficients under pressure to 10 000 atmospheres, and results were presented and discussed for self-diffusion in carbon disulfide. The method has been applied to five carbon disulfide-hydrocarbon mixtures: CS₂-*n*-heptane at 0°, 20°, and 40°C; CS₂-2,4 dimethylpentane at 20° and 40°C; CS₂-toluene at 20°C.

Results are also presented for the system CS₂-chlorobenzene in two concentrations, CS₂-*n*-butanol, and CS₂-iso-butanol.

In each case S³⁵ tagged CS₂ was used, and the mole fraction CS₂ in both radioactive and nonradioactive cells was 0.50, except for one isotherm in the system chlorobenzene-CS₂.

The S³⁵ tagged CS₂ was obtained from Tracerlab. The *n*-heptane, *n*-octane, 2,4 dimethylpentane, and methylcyclohexane were Phillips pure grade. The toluene, chlorobenzene, and alcohols were Eastman Kodak pure grade, and the cp carbon disulfide was obtained from J. T. Baker Chemical Company.

* This work was supported in part by the U. S. Atomic Energy Commission.

¹ R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 267 (1953).

The method of measuring the concentration and of calculating the diffusion coefficient is described in detail in the previous work¹⁻³ and will not be discussed here.

The method of operation and for calculation of the diffusion coefficient from the experimental data is discussed in reference 1. The kinetic theory of liquids, the possible pressure effects on the structure of liquids in general, and the mechanism for calculation of the activation volume ($\Delta V^\ddagger$), the activation enthalpy ($\Delta H^\ddagger$), and the entropy of activation ($\Delta S^\ddagger$) above that at atmospheric pressure ($\Delta S_0^\ddagger$) are outlined completely in reference 1.

The results of the present study will be discussed in terms of these concepts.

RESULTS

The diffusion coefficients are shown in Tables I-IX. Each system is discussed in detail below, but it is desirable first to outline the premises upon which the discussion is based.

An understanding of, and cohesion among, the wide variety of results obtained in this study depends upon

² K. D. Timmerhaus and H. G. Drickamer, J. Chem. Phys. 19, 1242 (1951).

³ W. L. Robb and H. G. Drickamer, J. Chem. Phys. 19, 1504 (1951).

TABLE I. Measured diffusion coefficients for 50 percent (mole) CS₂ in *n*-C₇H₁₆.^a

Temp. °K	Pressure atmos	Effective cell length cm	Observed $D \times 10^5$ cm ² /sec
293	150	0.504	2.88
293	5000	0.611	0.515
293	7000	0.611	0.375
273	100	0.504	2.00
273	1200	0.504	1.46
273	3050	0.557	0.455
293	600	0.504	2.75
293	1200	0.504	2.53
293	2800	0.557	1.18
313	100	0.504	4.36
313	1200	0.504	4.17
313	3500	0.557	1.92
313	5200	0.611	1.01
313	7000	0.611	0.526
313	10 000	0.665	0.43

^a Maximum deviation in reproducibility 10 percent. Average deviation 5 percent.

having a satisfactory molecular picture of a liquid which consists of nonspherically symmetrical molecules. The various systems investigated will be discussed with the picture in mind that motion in a liquid, (or the residence time of a molecule) depends largely upon the free volume between molecules (or the intensity and shape of the force field around a given molecule).

The variation of the diffusion coefficient with pressure should depend upon the free volume change in the following manner: (1) The change in the diffusion coefficient for a given change in pressure will depend upon the amount by which the free volume has been decreased. That is, the rate of change of the intensity of the force field around a molecule (and also the rate of change of the diffusion coefficient) will depend upon the rate of change of the free volume. In general, as the free volume is decreased the diffusion coefficient will also decrease. (2) It is clear that the shape of the molecules involved will be of importance in determining the effect of free volume on D . That is, depending upon the shape of the molecules, it is conceivable that a given orientation will have a higher probability for motion than some other orientation. As pressure is increased and the force fields surrounding each molecule are intensified, the probability of the preferred orientation for motion may

TABLE II. Measured diffusion coefficients for 50 percent (mole) CS₂ in *n*-C₈H₁₈.^a

Temp. °K	Pressure atmos	Effective cell length cm	Observed $D \times 10^5$ cm ² /sec
293	200	0.504	2.82
293	600	0.504	2.59
293	1200	0.504	2.62
293	2000	0.557	1.45
293	4000	0.611	0.628
293	6100	0.611	0.282

^a Maximum deviation in reproducibility 10 percent. Average deviation 5 percent.

be decreased. Thus, we see that the residence time may be increased by decreasing the free volume if the molecular shape is such that the probability of motion is a function of orientation. This consideration is probably unimportant for spherically symmetrical molecules or for small molecules surrounded by larger ones. Carbon disulfide in organic solutions, as studied in this investigation, would probably fall into the second classification. (3) This third point is of importance only for nonspherically symmetrical molecules; however, this is the only type we are concerned with in the present

TABLE III. Measured diffusion coefficients for 50 percent (mole) CS₂ in 2,4 dimethylpentane.^a

Temp. °K	Pressure atmos	Effective cell length cm	Observed $D \times 10^5$ cm ² /sec
293	200	0.504	3.15
293	1200	0.504	1.78
293	3500	0.557	1.22
293	6700	0.611	0.479
313	200	0.504	4.46
313	900	0.504	3.52
313	2000	0.557	2.37
313	3500	0.557	1.80
313	4900	0.611	1.26
313	7000	0.611	0.842
313	7000	0.611	0.763
313	10 200	0.665	0.657

^a Maximum deviation in reproducibility 10 percent. Average deviation 5 percent.

TABLE IV. Measured diffusion coefficients for 50 percent (mole) CS₂ in toluene.^a

Temp. °K	Pressure atmos	Effective cell length cm	Observed $D \times 10^5$ cm ² /sec
293	1	0.504	1.93
293	50	0.504	1.93
293	300	0.504	1.49
293	900	0.504	0.742
293	3300	0.557	0.575
293	7150	0.611	0.530
313	200	0.504	4.03
313	900	0.504	1.97
313	1500	0.665	1.49
313	3500	0.557	0.850
313	5750	0.611	0.710
313	9100	0.665	0.669

^a Maximum deviation in reproducibility 10 percent. Average deviation 5 percent.

study. We may speak of the "shape" of a force field since it is probably true that nonspherically symmetrical force fields are associated with nonspherically symmetrical molecules. In fact, this is precisely what we mean when we speak of a nonspherically symmetrical molecule (since physical measurements of molecular properties are actually measures of the properties of their associated force fields). When free volume is decreased, i.e., the force fields intensified, it is not necessarily true that the "shape" of the force field remains the same. It may be the case that the force field is

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deformed in spite of the fact that sufficient energy is not applied to deform the molecule with which it is associated. In other words, we change the degree of "steric hindrance" on an intermolecular scale. The net effect could be to increase the necessity of there being a favorable orientation for migration with a corresponding increase in the residence time.

In the discussions to follow an occasional reference is made to a "lattice" or "packing" in the liquid. We do not wish to imply the existence of any structure which

TABLE V. Measured diffusion coefficients for 50 percent (mole) CS₂ in methylcyclohexane.^a

Observed $D \times 10^4$ cm ² /sec	Temp. °K	Pressure atmos	Effective cell length cm	Observed $D \times 10^4$ cm ² /sec
3.15	273	50	0.504	2.37
1.78	273	1200	0.504	0.621
1.22	273	3000	0.557	0.236
0.479	293	50	0.504	2.65
4.46	293	900	0.504	1.83
3.52	293	3000	0.557	0.585
2.37	293	7000	0.611	0.192
1.80	313	200	0.504	3.00
1.26	313	900	0.504	1.97
0.842	313	2000	0.557	1.34
0.763	313	4000	0.557	0.965
0.657	313	5000	0.611	0.690
	313	6300	0.611	0.540
	313	7750	0.665	0.485
	313	10 000	0.665	0.351

^a Maximum deviation in reproducibility 10 percent. Average deviation 5 percent.

TABLE VI. Measured diffusion coefficients for 50 percent (mole) CS₂ in chlorobenzene.^a

Observed $D \times 10^4$ cm ² /sec	Temp. °K	Pressure atmos	Effective cell length cm	$D \times 10^4$ cm ² /sec
1.93	293	218	0.504	2.60
1.93	293	1530	0.504	0.943
1.49	293	3500	0.557	0.870
0.742	293	7000	0.611	0.330
0.575	313	200	0.504	4.63
0.530	313	900	0.504	2.59
4.03	313	2000	0.504	1.84
1.97	313	2000	0.504	2.02
1.49	313	3000	0.557	2.18
0.850	313	3500	0.557	1.66
0.710	313	4850	0.557	1.05
0.669	313	8200	0.665	0.422
	313	10 000	0.665	0.254

^a Maximum deviation in reproducibility 10 percent. Average deviation 5 percent.

would be macroscopically observable. Rather, we mean that the free volume is such that the probability of the most favored orientation for motion of the organic molecules has decreased to a point where their residence time is long as compared with that of the CS₂ molecules. The residence time in normal liquids composed of single, free moving molecules, is of the order of 10⁻¹³ second. If this were reduced, by say a factor of 10, for the organic molecules through suitable intensification of force fields as described above, the motion would still be highly

TABLE VII. Measured diffusion coefficients for 20 percent (mole) CS₂ in chlorobenzene.^a

Temp. °K	Pressure atmos	Effective cell length cm	$D \times 10^4$ cm ² /sec
313	200	0.504	3.52
313	900	0.504	2.42
313	900	0.504	1.78
313	2000	0.504	1.29
313	2800	0.557	1.30
313	4400	0.557	0.912
313	7000	0.611	0.565

^a Maximum deviation in reproducibility 10 percent. Average deviation 5 percent.

rapid and chaotic on a macroscopic scale. However, the organic molecules would present a relatively long-lived "lattice" to inhibit CS₂ migration. When we speak of a "stable lattice," "packing," or "structure," we mean that the most probable configuration does not change greatly with pressure.

The discussion above concerning the relation between free volume and motion in liquids is meant to apply to solutions not subject to hydrogen bonding, solvation, or any other phenomena which tend to bond molecules together.

CARBON DISULFIDE IN NORMAL HEPTANE AND IN NORMAL OCTANE

The data are shown in Fig. 1 plotted as $\ln D$ as a function of pressure for the three isotherms 0°, 20°, and 40°C.

From the general shape of the isotherms in Fig. 1 it appears that in the low pressure range (up to about 2000 atmos at 40°) the heptane structure is quite loose and does not inhibit the movement of CS₂ molecules so that we have essentially self-diffusion in CS₂. As pressure is further increased the presence of the heptane becomes important and the structure begins to rapidly "close in" as shown by the rapid decline of D with pressure in the range 2000 to 7000 atmos at 40°C. Beyond 7000 atmos, however, the isotherm flattens out indicating a fairly stable heptane packing, and CS₂ moves through the interstices. The diffusion coefficient in the 7000 to

TABLE VIII. Measured diffusion coefficients for 50 percent (mole) CS₂ in *n*-butanol.^a

Temp. °K	Pressure atmos	Effective cell length cm	$D \times 10^4$ cm ² /sec
293	200	0.504	3.06
293	1500	0.504	1.21
293	3500	0.557	0.714
293	7000	0.611	0.192
313	210	0.504	4.29
313	950	0.504	2.10
313	2000	0.504	1.42
313	3500	0.557	1.21
313	5450	0.665	0.963
313	7000	0.611	0.534
313	9000	0.665	0.315

^a Maximum deviation in reproducibility 10 percent. Average deviation 5 percent.

TABLE IX. Measured diffusion coefficients for 50 percent (mole) CS₂ in *i*-butanol.^a

Temp. °K	Pressure atmos	Effective cell length cm	$D \times 10^5$ cm ² /sec
293	200	0.504	2.10
293	2000	0.504	1.03
293	3500	0.557	0.876
293	5000	0.557	0.454
293	5650	0.611	0.235
313	200	0.504	2.95
313	1500	0.504	2.34
313	2500	0.557	1.84
313	3500	0.557	0.494
313	3500	0.557	0.565
313	5000	0.557	0.368
313	5700	0.611	0.333
313	8000	0.611	0.232

^a Maximum deviation in reproducibility 10 percent. Average deviation 5 percent.

10 000 atmos range at 40° for CS₂ in *n*-C₇ is about a factor of 5 less than that for pure CS₂ at the same temperature and pressure. This then is the factor by which the heptane structure inhibits the migration of CS₂ molecules in the high pressure range.

Diffusion coefficients were also determined for a 50 mole percent solution of carbon disulfide in normal octane along a 20° isotherm and are plotted in Fig. 1 with the isotherms for *n*-heptane. Comparing the two 20° isotherms it is seen that they are both identical in shape, with that for *n*-C₈ being slightly lower and tending to diverge further below the *n*-C₇ curve as pressure is increased. This observation fits in quite well with the analysis of the *n*-C₇ isotherms as given above. The addition of an extra -CH₂- to the *n*-heptane chain is seen merely to emphasize the effect of pressure on *D*. Thus, the octane structure becomes important in limiting the CS₂ diffusion at a slightly lower pressure than does the heptane structure and likewise, the octane reaches the "stable" configuration at a somewhat lower pressure.

In speaking of the heptane or octane structure it is not meant to imply that there exists a rigid static structure through which the CS₂ molecules must find their way.

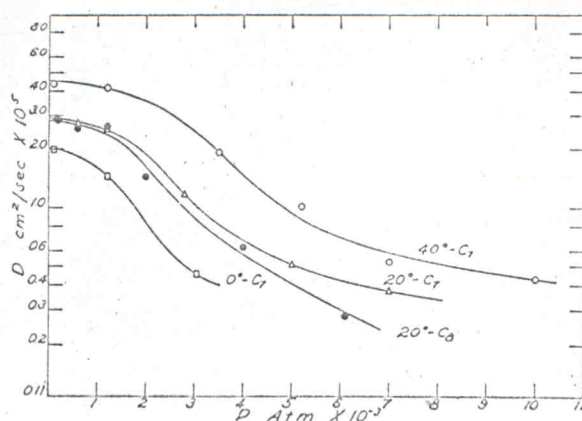


FIG. 1. Diffusion coefficient versus pressure. Systems: CS₂-*n* heptane, CS₂-*n* octane.

However, for purposes of discussion it is convenient to think of the long-chain molecules as being static relative to the movement of CS₂ molecules for an infinitesimal time; keeping in mind that the long chains are always in a state of random motion characteristic of liquid molecules. Thus, with this sort of a picture in mind one might, as an extreme case, think of a type of diffusion analogous to interstitial diffusion in crystalline solids. The analysis of the shape of the *n*-C₇-CS₂ isotherms given above provides evidence that a type of "interstitial" mechanism does exist in the high pressure range (beyond 7000 atmos at 40°).

A consideration of the change in activation entropy from that at atmospheric pressure further substantiates the existence of an interstitial type mechanism in the high pressure range. Values of $\Delta S_P^\ddagger - \Delta S_0^\ddagger$ are plotted as a function of pressure along a 20° isotherm in Fig. 2. The activation entropy increases rapidly beyond a pressure of 1000 atmos to a maximum of 9 cal/°K/mole,

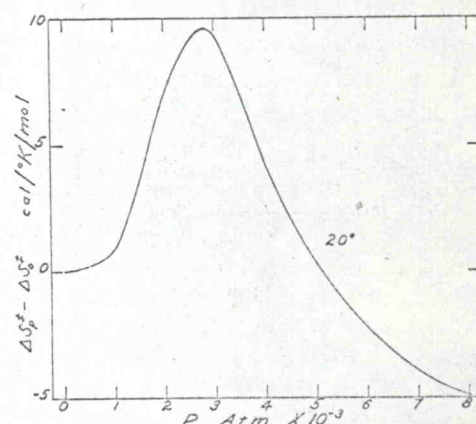


FIG. 2. Entropy of activation versus pressure. System: CS₂-*n* heptane.

above that at atmospheric pressure, at 2800 atmos. The difference then decreases and becomes negative so that at 8000 atmos the activation entropy is 5 eu below that at 1 atmos. The curve is leveling in such a manner that it would probably be asymptotic to about -6 eu at higher pressure. We shall assume that Eyring's⁴ estimate that the activation entropy is essentially zero for atmospheric pressure diffusion is valid for this solution of *n*-C₇ in CS₂.

As pressure is increased from atmospheric, the heptane structure is at first loose enough so as to not greatly inhibit the diffusion of CS₂ and we find the activation entropy increasing slowly due to increasing order in the initial state. As the pressure is increased beyond 1000 atmos the presence of the heptane becomes of more importance and the liquid attains a higher degree of order and lower entropy level in the normal state. Therefore, the entropy change associated with a

⁴ Eyring, Laidler, and Glasstone, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

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molecule entering the activated state is increasing. When that pressure is approached where the maximum value of $\Delta S_P^\ddagger - \Delta S_0^\ddagger$ occurs, the limitations imposed by the heptane become of increasingly greater consequence. Finally, at the maximum, the increased order of the normal state is offset by the compactness of the heptane structure which requires that the probability of a CS₂ molecule entering the activated state depends upon its orientation. Thus, the relative entropy of the activated state is decreased. This effect becomes more and more pronounced as pressure is increased until finally the activation entropy becomes negative (since we have assumed $\Delta S_0^\ddagger = 0$). This picture might be more clearly seen by recalling that for the self-diffusion in CS₂¹ we accounted for high entropies of activation by pointing out that for a molecule to enter the activated state it must break loose from an ordered configuration, thus increasing its degrees of freedom. In this case, however, a diffusing molecule must pass through a hole in the heptane "lattice" and the possible directions it may take are limited compared to those available in pure CS₂. Thus, we see that the limitations imposed by the heptane structure are so stringent that a molecule in the

TABLE X. $\Delta F^\ddagger - \Delta F_0^\ddagger$ for *n*-C₇-CS₂ at 20°C.

P (atmos)	$\Delta F^\ddagger - \Delta F_0^\ddagger$ (cal/mol)
1000	31
2000	205
3000	526
4000	775
6000	1070
8000	1150

activated state for diffusion has fewer degrees of freedom than one in the initial state and thus the entropy of activation is negative.

The curves of activation enthalpy *versus* pressure show the same maximum as does the entropy curve. Activation enthalpies are plotted in Fig. 3 for 282, 293, and 302°K. The dashed curve for 293° was estimated in order that the entropy data could be calculated using values of *D* at 293°K. The similarity of the curves of $\Delta H^\ddagger$ *vs* *P* and of $\Delta S_P^\ddagger - \Delta S_0^\ddagger$ *vs* *P* is consistent with Levi's observation⁶ that a high heat of activation is associated with a high entropy of activation and vice versa; again, we would expect $\Delta F^\ddagger$ to remain substantially constant. $\Delta F_P^\ddagger - \Delta F_0^\ddagger$ for the 20° isotherm was calculated from the relation $\Delta F = \Delta H - T\Delta S$ and is tabulated in Table X.

It was assumed above that $\Delta S_0^\ddagger \cong 0$; therefore, $\Delta F_0^\ddagger = \Delta H_0^\ddagger = 3840$ cal/mole. On this basis then, the free energy of activation increases by only 30 percent in the 8000 atmosphere ranges. It is interesting to note that $\Delta F^\ddagger$ increases continuously with pressure and does not go through a maximum as do both $\Delta S^\ddagger$ and $\Delta H^\ddagger$.

⁶ D. L. Levi, Trans. Faraday Soc. 42a, 152 (1946).

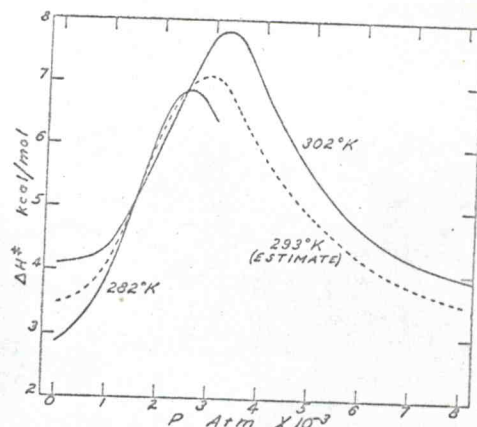


Fig. 3. Enthalpy of activation *versus* pressure. System: CS₂-*n* heptane.

The ratios of the activation volume to the molal volume for the three heptane isotherms and for the octane isotherm are plotted as a function of density in Fig. 4. In making these calculations the necessary compressibility and density data were estimated by assuming the solutions to be ideal and adding the properties of the pure components in proportion to their volume percent in solution.

In the very low density region of Fig. 4 it is seen that the activation volume is slightly negative. The truth of the matter is probably that the activation volume is zero and the negative value arises purely as a consequence of the difficulty in accurately determining the slope $\partial \ln D / \partial p$ at atmospheric pressure. $\Delta V^\ddagger / V$ rises slowly at first and then more rapidly to reach a maximum, at 40°C, of 18.5 percent of the molal volume at a density of about 1.02 g/cc; the ratio then decreases and levels out to a value of 3 percent at a density of 1.12 (*P* = 8500 atmos). This same trend is also shown by the remaining isotherms. The maximum at 0° is 19 percent for $\rho \cong 0.99$, that at 20° is 15.5 for $\rho \cong 0.99$, and for the normal octane the maximum activation volume is 18.5 percent of the molal volume at $\rho \cong 0.97$.

The looseness of the heptane structure in the low pressure range is again apparent from a consideration of the activation volume. The slow initial rise of $\Delta V^\ddagger / V$ with increasing density is analogous to that found for

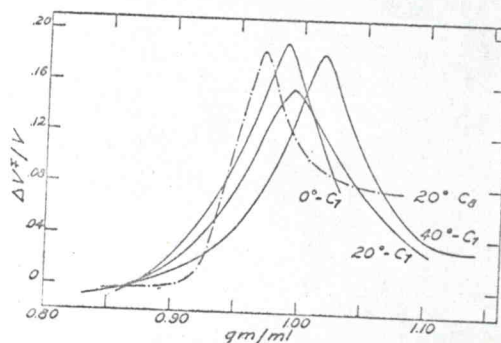


Fig. 4. Activation volume *versus* density. System: CS₂-*n* heptane.

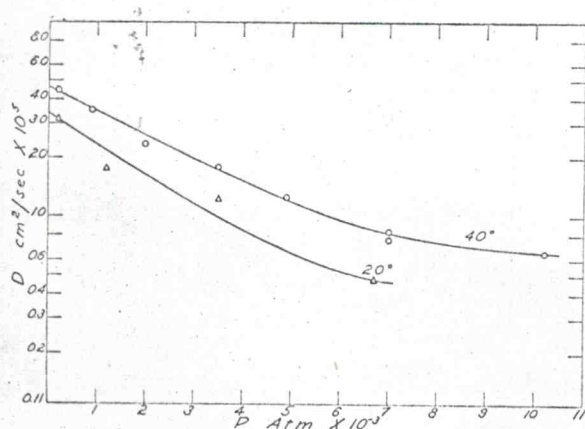


FIG. 5. Diffusion coefficient versus pressure.
System: CS_2 -2,4 dimethylpentane.

CS_2 and indicates the existence of a sufficient number of holes for diffusion to occur with only a slight local expansion. As density is increased the heptane molecules begin to impede the CS_2 to a greater extent and must be pushed back to permit diffusion. Therefore, we find the activation volume increasing. Where the activation volume begins to decrease and the diffusion coefficient drops off rapidly, the structure becomes "stable" and the CS_2 molecules tend to diffuse through existing holes. At this point the activation volume settles down to some constant fraction of the molal volume. The final, asymptotic value of $\Delta V^\ddagger/\bar{V}$ is greater at the higher temperature, being 3 percent at 40° and about 2 percent at 20° for $n\text{-C}_7$. The value for $n\text{-C}_8$ at 20° is much higher, about 7 percent.

CARBON DISULFIDE IN 2,4 DIMETHYLPENTANE

Diffusion coefficients were determined as a function of pressure along two isotherms in a 50 mole percent solution of carbon disulfide and 2,4-dimethylpentane, ($i\text{-C}_7$). This system was studied in order that a comparison

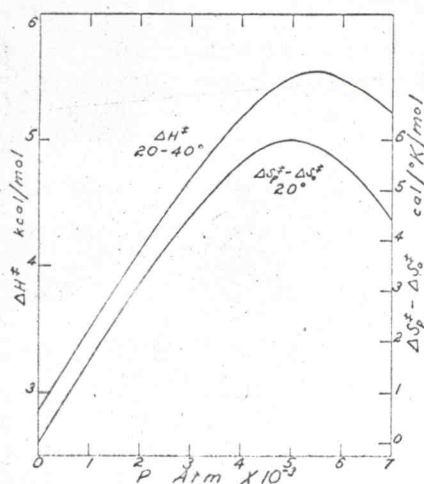


FIG. 6. Enthalpy and entropy of activation versus pressure.
System: CS_2 -2,4 dimethylpentane.

could be made with the data for n -heptane in an effort to ascertain the effects of chain branching on the structure in isomeric liquid paraffins. The data obtained are shown graphically as $\ln D$ plotted as a function of P in Fig. 5.

The atmospheric pressure diffusion coefficient at 40° is the same in both the iso and normal C_7 , 4.6×10^{-4} cm^2/sec . Thus, at atmospheric pressure both structures present the same impediment to CS_2 migration. As pressure is increased, however, the iso structure immediately begins to close in as evidenced by the steady decline of $\ln D$ from atmospheric pressure. With further increase of pressure the relatively stable configuration of the iso-heptane packing takes form steadily and the slope of the curve decreases.

Compressibility data were not available for 2,4-dimethylpentane so that it was necessary to use n -heptane compressibilities. Bridgman⁶ has shown that the compressibility varies only slightly among isomeric six-carbon paraffins.

The change in activation entropy with pressure is plotted as a function of pressure along a 20°C isotherm in Fig. 6. It is seen that as pressure is increased the

TABLE XI. $\Delta F_P^\ddagger - \Delta F_0^\ddagger$ for CS_2 in $i\text{-C}_7$ at 20°C .

P (atmos)	$\Delta F_P^\ddagger - \Delta F_0^\ddagger$ (cal/mole)
1000	181
2000	366
3000	544
5000	879
7000	1065

activation entropy increases, almost linearly, and reaches a maximum of 6 $\text{cal}/^\circ\text{K}/\text{mole}$, greater than that at 1 atmos, at 5000 atmos; it then drops off until at 7000 atmos it is only 4.4 eu greater than at atmospheric pressure. The shape of this curve indicates that as pressure is increased from atmospheric the iso-heptane structure is of immediate importance, contrary to the case for the normal isomer, and the liquid becomes more ordered, lowering the entropy level of the normal state. Thus, we find that the entropy change for a molecule to enter the activated state is increasing. At the pressure where the maximum value of $\Delta S_P^\ddagger - \Delta S_0^\ddagger$ is observed, (5000 atmos), the iso-heptane "lattice" has formed to such an extent that the degrees of freedom of a molecule activated for diffusion are restricted to a point where further increase in pressure decreases the activation entropy. When the pressure is increased beyond 5000 atmos the limitations on the possible orientations of an activated CS_2 molecule imposed by the packing increase at a greater rate than does the order in the normal state and the activation entropy decreases. From an analogy with the normal heptane data it is anticipated that if the pressure were increased beyond 7000 atmos, the $i\text{-C}_7$

⁶ P. W. Bridgman, *The Physics of High Pressure* (Macmillan Company, New York, 1931).

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The activation enthalpy varies in a similar manner with pressure as does the activation entropy. $\Delta H^\ddagger$ is plotted as a function of pressure in Fig. 6.

We shall again assume $\Delta S_0^\ddagger \cong 0$ so that $\Delta F_0^\ddagger = \Delta H_0^\ddagger = 2860$ cal/mole. It is seen from Table XI below that the free energy of activation increases continuously with pressure so that its value at 7000 atmos is 37 percent greater than that at 1 atmos. $\Delta F_P^\ddagger - \Delta F_0^\ddagger$ was calculated from the relationship $\Delta F = \Delta H - T\Delta S$.

The activation volume is shown in Fig. 7. From the initial slope of the curve of $\ln D$ vs P (Fig. 8) we know that the iso-heptane impedes the migration of CS₂ even in the very low pressure range. The structure remains flexible enough, however, so that it may be deformed to permit diffusion and we observe a relatively high activation volume. At the pressure where the maximum $\Delta V^\ddagger/\bar{V}$ occurs (2500 atmos) a point is reached where

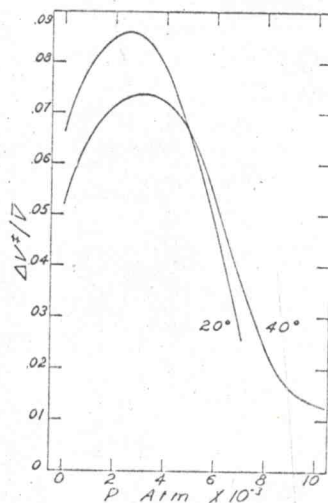


FIG. 7. Activation volume versus pressure. System: CS₂-2,4 dimethylpentane.

further compression strengthens the structure to such an extent that it will not yield easily and the activation volume begins to decrease as the diffusion takes place more and more through existing holes. The "stable" (stable in the sense that the most probable configuration does not vary greatly with pressure) structure of the i -C₇ is formed much more slowly with pressure than is that of the normal isomer. Thus, the limitations imposed upon the degrees of freedom of an activated molecule by the i -C₇ structure do not increase as rapidly with pressure as does the degree of order in the normal state until a much higher pressure is reached (5000 atmos). This is why the activation entropy continues to increase with pressure in the range 2500 to 5000 atmos even though diffusion is taking place more and more through existing holes and the activation volume is decreasing.

CARBON DISULFIDE IN TOLUENE

The logarithm of the diffusion coefficient for carbon disulfide in toluene is plotted as a function of pressure

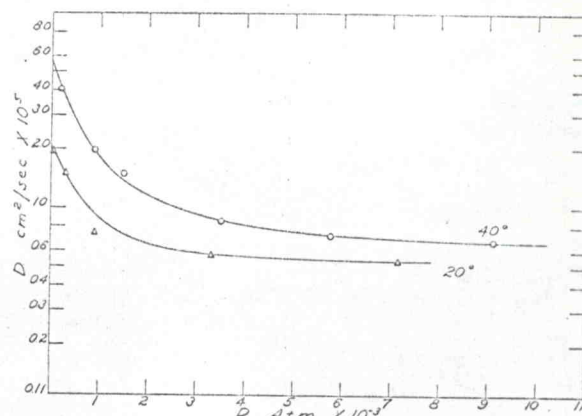


FIG. 8. Diffusion coefficient versus pressure. System: CS₂-toluene.

along 20 and 40°C isotherms in Fig. 8. The atmospheric pressure D at 40° is relatively high, 5.6×10^{-5} cm²/sec as compared with 4.6×10^{-5} for the three systems previously discussed (pure CS₂, n -C₇-CS₂, i -C₇-CS₂) but drops off very rapidly with increasing pressure. At 3500 atmos the value is 0.85×10^{-5} , and with further compression it levels to become asymptotic to about 0.65×10^{-5} . With the initial application of pressure the toluene molecules, which are known to exist in the solid as flat plates, immediately begin to orient and impede diffusion of CS₂. As the solution is further compressed the orientation of the toluene structure increases until finally a configuration is reached wherein further compression does not alter the rate of CS₂ migration through holes in the toluene "lattice." The packing in the toluene is probably made up of flat molecular plates oriented parallel to each other. Once this configuration has been achieved, further compression will not appreciably alter it except that the distance between layers of plates may be decreased.

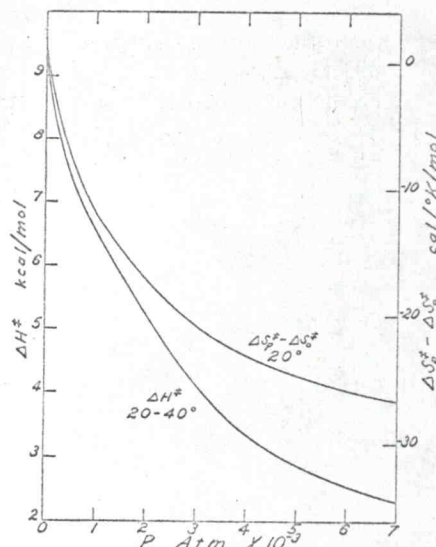


FIG. 9. Enthalpy and entropy of activation versus pressure. System: CS₂-toluene.

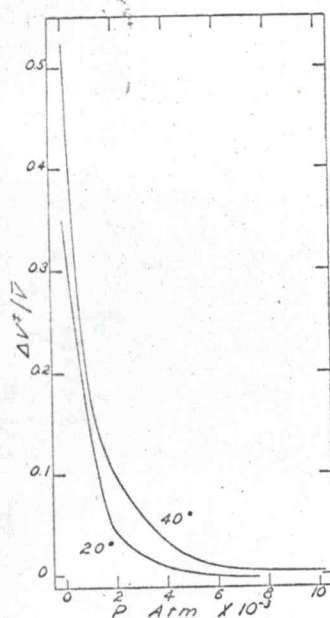


FIG. 10. Activation volume versus pressure. System: CS_2 -toluene.

Compressibility data were not available for toluene. It was assumed that the compressibility of toluene would vary with pressure similarly to that for chlorobenzene, and also that its value at atmospheric pressure would be the same as the value for benzene. Since data are available for benzene and chlorobenzene,⁶ the toluene compressibility was estimated on the basis of these two assumptions.

The change in activation entropy with pressure is plotted as a function of pressure in Fig. 9. The activation entropy decreases rapidly at first and then more slowly as pressure is increased. At 7000 atmos it is 26.7 cal/°K/mole less than the value at atmospheric pressure. The continual decrease of $\Delta S^\ddagger$ indicates that the restrictions imposed by the toluene on the most favorable orientation of an activated molecule are increasing at a rate greater than the rate at which the degrees of freedom of a molecule in the normal state are decreasing. The leveling of the curve of $\Delta S_P^\ddagger - \Delta S_0^\ddagger$ in the high

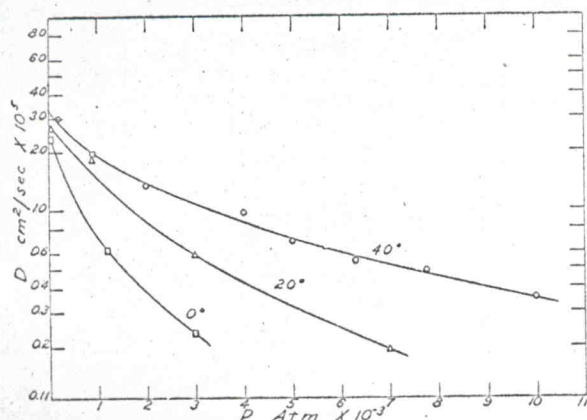


FIG. 11. Diffusion coefficient versus pressure. System: CS_2 -methylcyclohexane.

pressure range indicates that the toluene lattice (i.e., the most probable configuration at any time) is virtually stabilized and further compression does not appreciably alter the relative entropy levels of a molecule of CS_2 in the initial and activated states.

$\Delta H^\ddagger$ is shown graphically as a function of pressure in Fig. 9. Similarly to the entropy of activation, it decreases rapidly with increasing pressure at first and then slowly begins to level off. At 7000 atmos $\Delta H^\ddagger$ is 2.3 kcal/mole. The high value of the heat of activation at atmospheric pressure indicates that the process of activation involves a considerable distortion of the structure in the low pressure area. Since this is the case, then it must also follow that the entropy of the activated state must be greater than that of the normal state; that is, an activated molecule has gained degrees of freedom over one in the initial state. Therefore, the assumption of an essentially zero entropy of activation at atmospheric pressure is probably not applicable to this system.

An inspection of the curve of $\Delta V^\ddagger/\bar{V}$ plotted as a function of pressure in Fig. 10 substantiates the deduc-

TABLE XII. $\Delta F^\ddagger - \Delta F_0^\ddagger$ for CS_2 in toluene at 20°C.

P (atmos)	$\Delta F^\ddagger - \Delta F_0^\ddagger$ (cal/mole)
500	293
1000	484
2000	633
3000	689
4000	712
5000	719
6000	721
7000	721

tion that activation at atmospheric pressure involves a considerable distortion of the liquid structure. The activation volume is 50 percent of the molal volume at 40°C and 1 atm. It decreases at an extremely high rate with pressure to 18 percent at 1000 atmos and only 5 percent of the molal volume at 3500 atmos. Beyond 6000 atmos at 40° and 4500 atmos at 20°, the activation volume is constant at less than one percent of the molal volume. Allowing for errors in the calculations, the truth is probably that both isotherms level to a value of zero. Thus, it is seen that over the pressure range studied, the process of activation changes from being predominately one of structure deformation and hole formation to being mostly a matter of selecting favorably oriented molecules to diffuse through existing holes.

The change in the free energy of activation with pressure is quite small and $\Delta F^\ddagger$ becomes constant beyond 3000 atmos at 20°C. Values of $\Delta F^\ddagger - \Delta F_0^\ddagger$ are given in Table XII.

It was pointed out above that the assumption of a zero value for the entropy of activation at atmospheric pressure is probably not valid for this system. Thus, it is

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$\bar{V}^\ddagger$ plotted as a function of pressure. The deduced values at 20°C.

(cal/mole)

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pressure involves a change in structure. The molal volume at atmospheric pressure is extremely high and only decreases above atmospheric pressure. Beyond this, the activation volume of the molal volume decreases rapidly while $\Delta H^\ddagger$ and $\Delta S^\ddagger$ both increase at a high rate. The MCH molecules must tend to restrict or "trap" CS₂ molecules so that their entropy in the normal state becomes very low. Thus, we find that as the force fields are intensified (pressure increased) diffusion takes place more and more through existing holes, so that $\Delta V^\ddagger/\bar{V}$ decreases while the activation entropy increases because of the increasing order of the normal state. It must be assumed that in the lower pressure range (where $\Delta S^\ddagger$ is increasing rapidly) there are a sufficient number of holes available so that the probability of a molecule entering the activated state does not depend greatly upon its orientation. This mechanism becomes continually more prominent with pressure and gradually the number and size of holes is decreased so that certain orientations of the CS₂ molecule have a higher probability of migration than others. Thus, the entropy of the activated state begins to decrease and we find $\Delta S^\ddagger - \Delta S_0^\ddagger$ beginning to level. Beyond 4000 to 5000 atmos the ratio of the activation volume to the molal volume levels to become virtually constant at 0.07 at 20° and 0.04 at 40°. $\Delta S^\ddagger$ and $\Delta H^\ddagger$ also begin to level beyond this range and increase only slowly up to 7000 atmos. By comparison with the previous systems discussed it is anticipated that at some pressure beyond the range of our calculations $\Delta S_P^\ddagger - \Delta S_0^\ddagger$ would go through a maximum and then become asymptotic to some lower value.

activation with pressure constant beyond $\Delta F_0^\ddagger$ are given

assumption of a constant at atmospheric pressure. Thus, it is

impossible to estimate $\Delta F_0^\ddagger$. However, the constant value of $\Delta F^\ddagger - \Delta F_0^\ddagger$ is only 7.7 percent of $\Delta H_0^\ddagger$. ($\Delta H_0^\ddagger = 9400$ cal/mol.)

CARBON DISULFIDE IN METHYLCYCLOHEXANE

Three isotherms, 0°, 20° and 40°C, of D as a function of P are shown in Fig. 11.

In the previous discussion we assumed toluene molecules to exist in solution as flat plates. Cyclohexane is commonly thought to exist in one or the other of the familiar "chair" or "boat" forms. For this discussion, however, we shall assume only that the MCH molecule is a puckered type ring with one methyl group attached.

The atmospheric pressure diffusion coefficient for CS₂ in MCH at 40° is only 3.3×10^{-5} cm²/sec as compared with 5.6×10^{-5} in toluene. Thus, it is apparent that the puckered MCH ring inhibits migration of CS₂ at atmospheric pressure to a greater extent than does the flat toluene ring. The changes in diffusion mechanisms and structure which take place with increasing pressure can best be described for this system by considering the changes in activation enthalpy, entropy, and volume simultaneously.

TABLE XIII. $\Delta F_P^\ddagger - \Delta F_0^\ddagger$ for CS₂ in methycyclohexane at 20°C.

P (atmos)	$\Delta F_P^\ddagger - \Delta F_0^\ddagger$ (cal/mole)
1000	360
2000	645
3000	865
5000	1210
7000	1475

ultaneously. These variables have been calculated and are plotted as a function of pressure in Figs. 12 and 13.

The high value of the activation volume at atmospheric pressure, 20 percent of the molal volume at 40°C, indicates that there is a high degree of distortion and local expansion during activation for diffusion. As pressure is increased above atmospheric the activation volume decreases rapidly while $\Delta H^\ddagger$ and $\Delta S^\ddagger$ both increase at a high rate. The MCH molecules must tend to restrict or "trap" CS₂ molecules so that their entropy in the normal state becomes very low. Thus, we find that as the force fields are intensified (pressure increased) diffusion takes place more and more through existing holes, so that $\Delta V^\ddagger/\bar{V}$ decreases while the activation entropy increases because of the increasing order of the normal state. It must be assumed that in the lower pressure range (where $\Delta S^\ddagger$ is increasing rapidly) there are a sufficient number of holes available so that the probability of a molecule entering the activated state does not depend greatly upon its orientation. This mechanism becomes continually more prominent with pressure and gradually the number and size of holes is decreased so that certain orientations of the CS₂ molecule have a higher probability of migration than others. Thus, the entropy of the activated state begins to decrease and we find $\Delta S^\ddagger - \Delta S_0^\ddagger$ beginning to level. Beyond 4000 to 5000 atmos the ratio of the activation volume to the molal volume levels to become virtually constant at 0.07 at 20° and 0.04 at 40°. $\Delta S^\ddagger$ and $\Delta H^\ddagger$ also begin to level beyond this range and increase only slowly up to 7000 atmos. By comparison with the previous systems discussed it is anticipated that at some pressure beyond the range of our calculations $\Delta S_P^\ddagger - \Delta S_0^\ddagger$ would go through a maximum and then become asymptotic to some lower value.

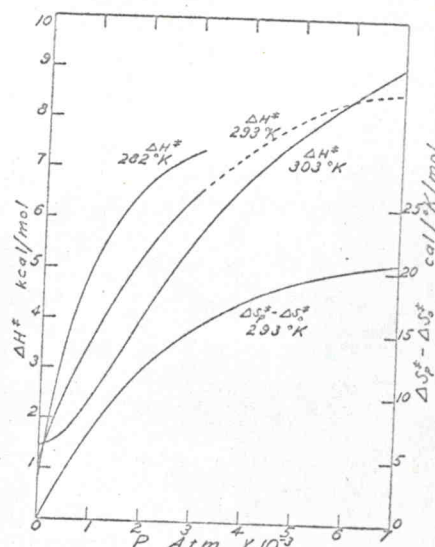
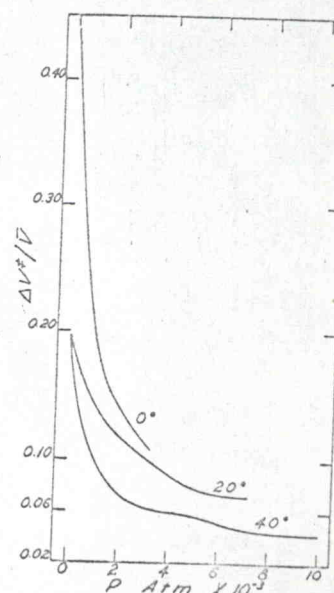


FIG. 12. Enthalpy and entropy of activation versus pressure. System: CS₂-methylcyclohexane.

We have consistently interpreted a decreasing activation entropy to mean that the packing of the organic molecules is ordered to such an extent that the probability of a CS₂ molecule becoming activated depends, with increasing pressure, more and more upon its

FIG. 13. Activation volume versus pressure. System: CS₂-methylcyclohexane.



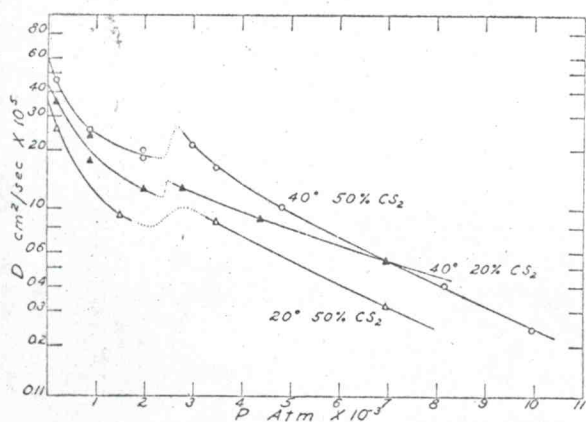


FIG. 14. Diffusion coefficients as a function of pressure. System: CS₂-chlorobenzene.

orientation. Or, in other words, that the hydrocarbon "lattice" has become a dominant factor. In toluene this situation was seen to exist over the entire pressure range. For CS₂ in *n*-C₇ it became prominent at 2800 atmos, while in *i*-C₇ the activation entropy did not begin to decrease until after 5000 atmos. For this system (MCH), although $\Delta S^\ddagger$ begins to level it is not seen to decrease in 7000 atmos. One might conclude then that for these four 7-carbon hydrocarbons, toluene molecules are the most easy to "align" with pressure, *n*-C₇ and *i*-C₇ are next in that order, with MCH being the most difficult.

The change in the free energy of activation from that at atmospheric pressure was calculated on the basis of the expression $\Delta F = \Delta H - T\Delta S$. From the values tabulated in Table XIII it is apparent that the free energy of activation is decidedly not constant with pressure, but

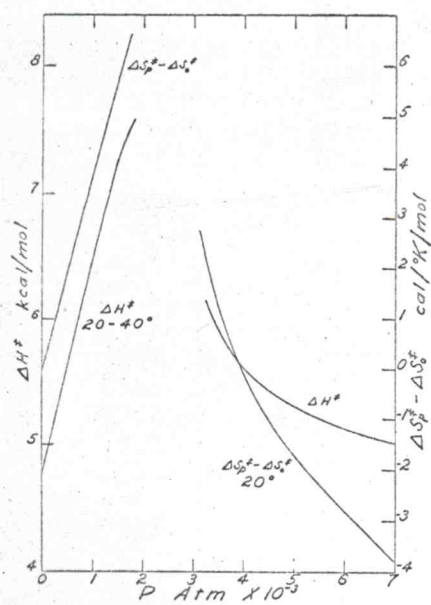


FIG. 15. Activation enthalpy and entropy as a function of pressure. System: CS₂-chlorobenzene.

rather, increases continuously. If it is valid to assume for this system that the entropy of activation is zero at 1 atmos, then $\Delta F_0^\ddagger = \Delta H_0^\ddagger = 1130$ cal/mole and the total increase in $\Delta F^\ddagger$ is 130 percent in 7000 atmos. However, in view of the high activation volume at 1 atmos it is probably not permissible to assume $\Delta S^\ddagger = 0$.

CARBON DISULFIDE IN CHLOROBENZENE

The diffusion coefficient was determined for carbon disulfide in two concentrations with chlorobenzene (PhCl). Two isotherms, 20 and 40°C, were obtained for a 50 mol percent solution and one 40°C isotherm was run for a solution of 20 mole percent CS₂ in PhCl. These data are plotted as a function of *P* in Fig. 14. The curves in this graph are immediately seen to be quite different from those previously discussed in that they show a discontinuity in the 2000 to 3000 atmos range. Below 2000 atmos and above 3000 atmos the isotherms appear to be quite normal. While the data were being obtained several attempts were made to determine *D* in the 2000 to 3000 atmos span, but reproducible results could not be obtained. It became apparent that some sort of structure transition takes place in this range which is extremely sensitive to pressure. Bridgman⁷ observed anomalous behavior on the part of PhCl in making determinations of freezing parameters for the compound. He concluded that there exists a second solid form which replaces the ordinary form as the absolutely stable one at high temperatures (125°C and above). At lower temperatures the liquid shows a tendency to not freeze on passing the normal melting line but to freeze instead to the new form when the unstable melting line of the new form is reached. This new form is unstable with respect to the normal form and may or may not arbitrarily "flop" irreversibly to the ordinary stable form. Bridgman found the appearance of such "flopping" to be quite unpredictable. The unstable form appeared at temperatures as low as 25°C, at which temperature the equilibrium pressure is 5000 atmos. There is no reason to believe that the discontinuity we observe in the $\ln D$ isotherms is due to any sort of freezing phenomenon; to the contrary, the diffusion coefficient on either side of the discontinuity is of the order of magnitude we expect in liquids.

Inspection of the curves of $\Delta S^\ddagger - \Delta S_0^\ddagger$, $\Delta H^\ddagger$, and $\Delta V^\ddagger/\bar{V}$, plotted as a function of pressure in Figs. 15 and 16, using the compressibility data of Bridgman⁸ shows that, in the low pressure range before the discontinuity, they are similar to those for methylcyclohexane in the same pressure range. The activation volume drops rapidly from about 44 percent of the molal volume at atmospheric pressure to about 5 percent at 2000 atmos. Both the 20 and 40° isotherms show changes of the same order of magnitude. At the same time the average activation enthalpy increases, virtually linearly, from 4.8 to about 7.8 kcal/mole, while $\Delta S^\ddagger$ also increases

⁷ P. W. Bridgman, Proc. Amer. Acad. Arts Sci. 74, 1, 399 (1940).

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linearly to 7 cal/°K/mole above its value at 1 atmos and 20°C. As in the case of MCH there is a high degree of structure distortion and local expansion at atmospheric pressure as shown by the large activation volume. The diffusion coefficient and $\Delta V^\ddagger/\bar{V}$, at 1 atmos are about twice as great in PhCl as they are in MCH and $\Delta H^\ddagger$ is a factor of 3.5 greater in the PhCl. The higher D and $\Delta V^\ddagger/\bar{V}$ indicate that the PhCl presents a structure at atmospheric pressure more susceptible to deformation than does the MCH.

As was the case with methylcyclohexane, the shape of the force fields associated with the chlorobenzene molecules must be such that decreasing the free volume leaves holes large enough for CS₂ diffusion. Thus, we find that as pressure is increased from one atmosphere, diffusion takes place more and more through these holes and the activation volume decreases. The holes must be of such number and shape that the probability of a CS₂ molecule becoming activated does not depend upon its orientation. This being the case, the entropy level of the activated state must not decrease as rapidly as does that of the initial state (which decreases due to the increasing order imposed by the decreasing free volume) for we find

TABLE XIV. $\Delta F^\ddagger - \Delta F_0^\ddagger$ for CS₂ in chlorobenzene at 20°C.

P (atmos)	$\Delta F^\ddagger - \Delta F_0^\ddagger$ cal/mol
500	410
1000	636
1750	812
3250	759
4000	893
5000	1050
7000	1340

the activation entropy increasing. This situation becomes increasingly predominant with pressure, at least as far as 2000 atmos.

There is undoubtedly some sort of radical structure transition which takes place in the 2000 to 3000 atmos range. We do not have sufficient data, however, to attempt an explanation.

Compressing beyond the transition range we find that the activation volume decreases rapidly to become constant at 9 percent of the molal volume at 20°C. The constant value of $\Delta V^\ddagger/\bar{V}$ at 40° is 10 percent. We also find $\Delta H^\ddagger$ and $\Delta S^\ddagger$ decreasing rapidly at first and then more slowly so that at 7000 atmos $\Delta H^\ddagger = 5$ kcal/mole and $\Delta S^\ddagger - \Delta S_0^\ddagger = -3.8$ cal/°K/mole.

In conformance with arguments presented for the previously discussed systems, we conclude that these changes in $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta V^\ddagger/\bar{V}$ indicate that the manner and amount by which the free volume has been decreased are such that a PhCl packing is forming with increasing pressure. As a consequence of this configuration, there is an increasing resistance to deformation and diffusion of CS₂ takes place more and more through existing holes. In addition, the number of available

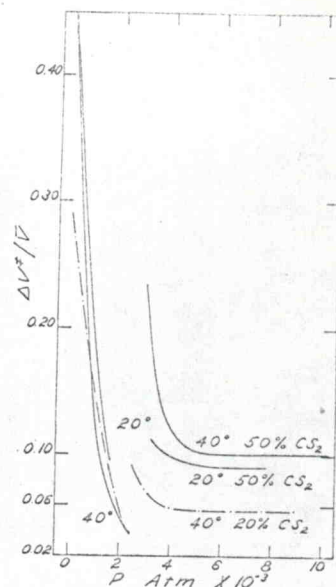


FIG. 16. Activation volume as a function of pressure. System: CS₂-chlorobenzene.

holes are limited so that the probability of a molecule entering the activated state is becoming more and more a function of its orientation. Thus, we see that $\Delta V^\ddagger/\bar{V}$ rapidly becomes constant and that the entropy of activation drops to a low level and appears to be approaching an asymptote.

The preceding discussion applies equally well to the diffusion of CS₂ in both 20 and 50 mole percent solutions of PhCl. The differences observed between the two concentrations are of degree rather than of kind. In the range below 2000 atmos the isotherms of $\Delta V^\ddagger/\bar{V}$ are the same for both concentrations within the accuracy of the data. The diffusion coefficient at 40°C in the 20 percent solution is lower than that in the 50 percent solution with its isotherm falling about half-way between the 20 and 40° isotherms for the more concentrated solution. Above 3000 atmos the ratio $\Delta V^\ddagger/\bar{V}$ becomes constant at a lower pressure in the dilute solution but at a lower value; 5.5 percent of the molal volume as compared to 10 percent in the 50 percent solution. The fact that the

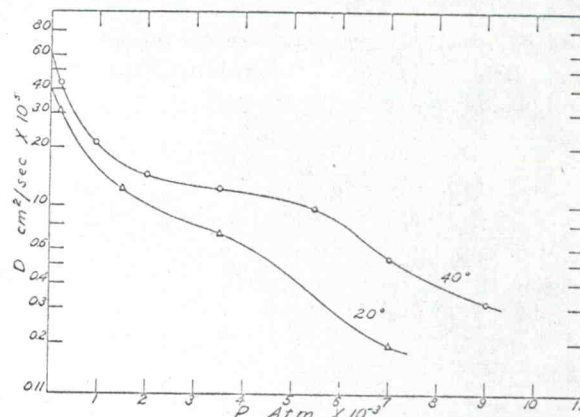


FIG. 17. Diffusion coefficients as a function of pressure. System: CS₂-n-butanol.

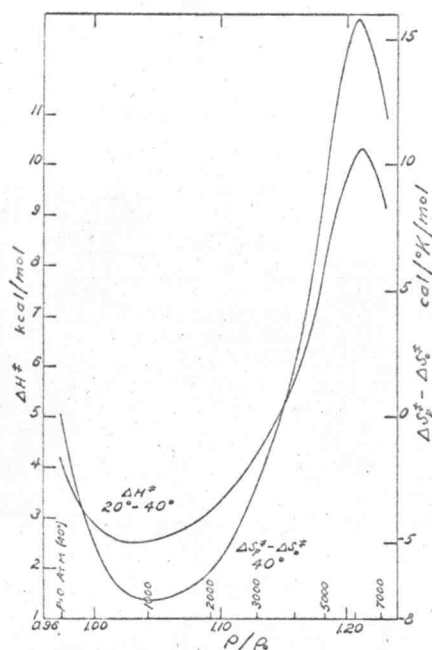


FIG. 18. Activation enthalpy and entropy as a function of reduced density. System: CS_2 - n -butanol.

ratio $\Delta V^\ddagger/\bar{V}$ is constant at a lower pressure in the 20 percent solution indicates that the "stable" structure is more easily formed when there is less CS_2 present.

From the relationship

$$\begin{aligned}\Delta F &= -T\Delta S + \Delta H \\ &= -T\Delta S + \Delta H,\end{aligned}$$

one might expect $\Delta F^\ddagger$ to be constant because of the close correspondence observed between changes in $\Delta H^\ddagger$ and in $\Delta S^\ddagger$. This is not the case, however, as can be seen from the values of $\Delta F^\ddagger - \Delta F_0^\ddagger$ tabulated in Table XIV below. In view of the high activation volume at one atmosphere it is probably not valid to assume $\Delta S_0^\ddagger \approx 0$ and set $\Delta F_0^\ddagger = \Delta H_0^\ddagger$. However, it is interesting to note that the maximum increase in the free energy of activation in 7000 atmos is only 28 percent of $\Delta H_0^\ddagger$ ($\Delta H_0^\ddagger = 4760$ cal/mole). Although $\Delta F_0^\ddagger$ rises over the entire pressure range, it does reflect the discontinuity in the 2000 to 3000 atmos span; but to a lesser extent than do $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

CARBON DISULFIDE IN NORMAL BUTANOL

Isotherms of the diffusion coefficient as a function of pressure were determined at 20 and 40°C in a 50 mole percent solution of carbon disulfide in n -butanol (n -BuOH). The data obtained are shown graphically in Fig. 17. Both isotherms are similar in shape and show a very rapid decline of $\ln D$ with pressure up to about 2000 atmos. In the range beyond 2000 atmos the slope decreases considerably so that a partial plateau is formed which extends to about 5500 atmos at 40°C. Beyond 5500 atmos $\ln D$ drops off steadily with pressure. The 20° isotherm does not definitely show a plateau; however,

the second derivative of $\ln D$ with respect to P does pass through zero. From the shape of these isotherms it appears that the structure is being rapidly altered to cause a large decline in D in the region below 2000 atmos. The structure then becomes relatively unaffected by pressure and remains so until about 5500 atmos (at 40°). At this point the decreasing free volume again becomes important and D decreases with pressure. One might expect that the alcohol is associated, but no attempt will be made to consider this in the interpretation of the data since neither the degree nor the effects of association are known.

The change in activation entropy from that at atmospheric pressure is plotted as a function of the reduced density, ρ/ρ_0 , in Fig. 18. The reduced density is the ratio of the density at any given pressure and temperature to that at 20°C and 1 atmos. Pressure is indicated along the abscissa to facilitate discussion of the curves. The activation enthalpy is plotted on the same graph for a similar reason. In this graph we can see both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ dropping rapidly with the initial application of pressure. $\Delta S^\ddagger - \Delta S_0^\ddagger$ reaches a minimum of about 7 cal/°K/mol below that at 1 atmos (40°C) and at the same time $\Delta H^\ddagger$ falls from 4.1 to a minimum of 2.5 kcal/mol. Both minima are at about 1000 atmos. Compressing beyond 1000 atmos we find both entities increasing rapidly to a sharp maximum at 6000 atmos. At this point the activation enthalpy is 10.3 kcal/mole and the activation entropy has risen to 15.8 eu above its value at one atmos.

The ratio of the activation volume to the molal volume is shown plotted as a function of the reduced density in Fig. 19. At one atmos and 40° the activation volume is 55 percent of the molal volume, and 43 percent at 20°. Both isotherms drop rapidly to minima of 7

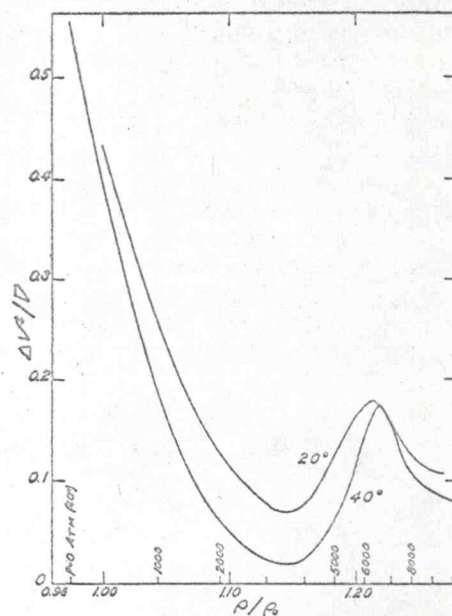


FIG. 19. Activation volume as a function of reduced density. System: CS_2 - n -butanol.

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percent at 20° and 3.5 percent at 40° at a pressure of about 3000 to 3500 atmos and then begin to increase again. A maximum of about 18 percent of the molal volume at 6000 atmos is shown at both temperatures.

Before carrying on with the discussion the reader is referred back to the curves of $\ln D$ vs P in Fig. 17. In drawing the curves it was reasonable that the 40° isotherm should be made a smooth curve through the experimental points and also, from observation of other systems, that the 20° isotherm should have a similar shape. However, the shapes of both curves could vary somewhat within the range of experimental error. $\Delta V^\ddagger/\bar{V}$, $\Delta H^\ddagger$, and $\Delta S^\ddagger - \Delta S_0^\ddagger$ vary critically with the slope of, and displacement between, the isotherms. Thus, it is felt that the maxima observed in these quantities at 6000 atmos may very well be a function of the manner in which the isotherms were drawn, within experimental error. No significance will be attached to these maxima without further proof of their existence. Similarly, the minima in $\Delta S^\ddagger - \Delta S_0^\ddagger$ and $\Delta H^\ddagger$ at 1000 atmos are open to doubt, and it is equally reasonable to

TABLE XV. $\Delta F^\ddagger - \Delta F_0^\ddagger$ for CS₂ in *n*-BuOH at 40°C.

P (atmos)	$\Delta F^\ddagger - \Delta F_0^\ddagger$ (cal/mole)
500	449
1000	680
2000	831
3000	953
5000	1014
7000	1437

assume that both of these variables rise continuously with pressure; the rise is very gradual in the low pressure range (up to about 2000 atmos).

The high value of the activation volume at atmospheric pressure indicates that a high degree of distortion and local expansion accompany the activation process. The decline in $\Delta V^\ddagger/\bar{V}$ can be interpreted to mean that the entropy level of the activated state is decreasing; that is, its degree of order is increasing. If $\Delta S^\ddagger$ increases continually from one atmosphere, then we must conclude that the entropy of the initial state decreases faster than does that of the activated state.

The rapid decline of the diffusion coefficient in the low pressure range indicates that the free volume is rapidly being taken up. Finally, as the 3000- to 3500-atmos range is reached, the free volume has been decreased by a sufficient amount, and in such a manner that a minimum is observed in the activation volume. Beyond this point the local expansion necessary for activation begins to be felt throughout a greater portion of the fluid due to the compactness of the packing. As is anticipated, the entropy of the activated state begins to rise more rapidly as shown by the sharp increase of $\Delta S^\ddagger - \Delta S_0^\ddagger$ in this range.

If we accept the validity of the maxima observed in $\Delta H^\ddagger$, $\Delta S^\ddagger - \Delta S_0^\ddagger$, and $\Delta V^\ddagger/\bar{V}$ at 6000 atmos, they may be interpreted as follows: A *n*-BuOH "lattice" formation

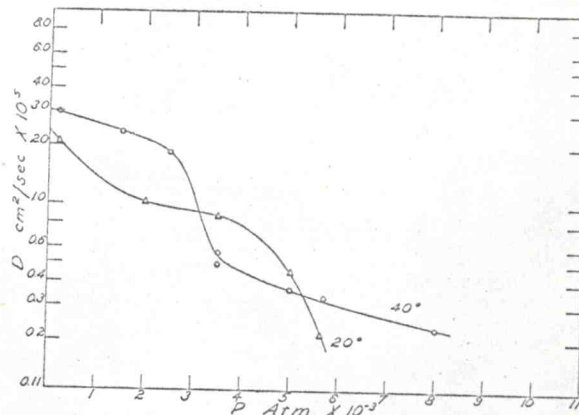


FIG. 20. Diffusion coefficients as a function of pressure. System: CS₂-*i*-butanol.

slowly takes place with increasing pressure. In the 6000-atmos range this packing is such that a CS₂ molecule has a higher probability of entering the activated state from certain orientations than from others. Thus, we find that beyond this range D begins to decrease more rapidly; the activation volume decreases because the structure resists deformation to a greater extent and diffusion takes place more and more through existing holes; and the activation entropy decreases because the entropy of the activated state decreases (certain orientations favored over others for activation).

We have observed in the data for this system the usual correspondence between $\Delta H^\ddagger$ and $\Delta S^\ddagger$. The change in the free energy of activation at various pressures from that at one atmosphere is tabulated in Table XV. $\Delta F^\ddagger$ is seen to rise continuously with pressure; its value at 7000 atmos is 35 percent of $\Delta H_0^\ddagger$.

CARBON DISULFIDE IN ISO-BUTANOL

The isotherms of $\ln D$ as a function of P for a 50 mole percent solution of carbon disulfide in iso-butanol (*i*-BuOH) are shown in Fig. 20. The uniqueness of the data for this system as compared to that for the other systems is immediately obvious upon inspection of the

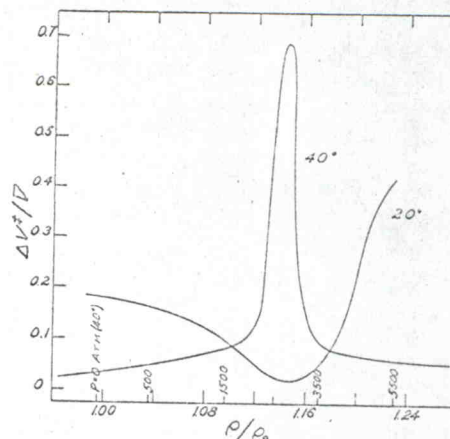


FIG. 21. Activation volume as a function of reduced density. System: CS₂-*i*-butanol.

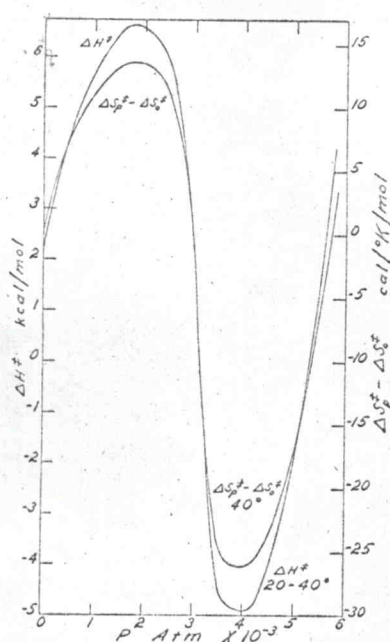


Fig. 22. Activation entropy and enthalpy as a function of reduced density. System: CS_2 -*i*-butanol.

graph. The 20° isotherm is quite similar to the isotherms obtained for CS_2 in *n*-BuOH in that $\ln D$ drops rapidly at first, settles to a partial plateau, and then continues to decline with pressure. The 40° isotherm, however, shows $\ln D$ to decrease only slowly with pressure up to 2500 atmos. Between 2500 and 3500 atmos D drops radically by a factor of three and then settles to once again decline slowly with pressure. The two isotherms cross at 3100 and 5250 atmos so that in this range D is actually less at 40° than at 20°C. The experimental points are such that there can be no question but what this is the true situation. It might be the case that the alcohol is associated but no attempt will be made to consider this in the interpretation of the data since neither the degree nor effects of association are known.

The activation volume for both the 20 and 40° isotherms is plotted as $\Delta V^\ddagger/\bar{V}$ versus reduced density in Fig. 21. The curve for the 20° isotherm is similar in nature to those for the *n*-BuOH isotherms and can be analyzed in the same manner. That is, the moderately high $\Delta V^\ddagger/\bar{V}$ at one atmosphere (18 percent of the molal volume) indicates a fair amount of distortion and local expansion associated with activation. The activation volume decreases continuously until a minimum of 2 percent of the molal volume is observed at 3000 atmos. (A minimum was found at this same pressure for the *n*-BuOH system.) Beyond 3000 atmos the ratio increases very rapidly to be about 0.40 at 5500 atmos. Here again we interpret the minimum in $\Delta V^\ddagger/\bar{V}$ as indicating a point where the free volume has been reduced in such a manner that the local expansion necessary for activation begins to be felt throughout a greater portion of the fluid.

At 40° the atmospheric pressure activation volume is

very low (2 percent of the molal volume). It increases very gradually with pressure to 9 percent at 2000 atmos, rises sharply to a peak of 69 percent at 3200 atmos, and then drops to 9 percent again at 4000 beyond where it decreases but gradually with pressure. The very low initial value of $\Delta V^\ddagger/\bar{V}$ indicates that, as in the case of *n*-C₇, the structure is initially very loose and permits activation with only a small amount of local expansion. Further, it must be the case that the molecular orientations and free volume are such that increasing pressure causes the local expansion for activation to be more generally felt throughout the liquid and the activation volume increases. It is certainly obvious that radical changes in structure must take place in order to cause the peak in $\Delta V^\ddagger/\bar{V}$ at 3200 atmos. With the limited data we have at this time, however, it would be pure conjecture to attempt to analyze the situation. In previous systems we have interpreted a decreasing activation volume in the high pressure range as indicating that an organic packing had been formed to such a degree that certain CS_2 orientations were preferred for activation and that migration took place more and more through existing holes. In conformance then, we must assume that the same situation prevails in this system after

TABLE XVI. $\Delta F^\ddagger - \Delta F_0^\ddagger$ for CS_2 in *i*-BuOH at 40°C.

<i>P</i> (atmos)	$\Delta F^\ddagger - \Delta F_0^\ddagger$ (cal/mole)
1000	66
2000	178
3000	543
3500	973
4500	1170
5750	1310

$\Delta V^\ddagger/\bar{V}$ passes through its peak and settles again to slowly decrease with pressure.

The curves of activation enthalpy and the change in activation entropy are plotted as a function of pressure in Fig. 22. The activation enthalpy (the most important factor in determining $\Delta S^\ddagger - \Delta S_0^\ddagger$) was calculated as an average value between the 20 and 40° isotherms of $\ln D$ vs *P*. Since these isotherms are so very dissimilar, it is doubtful whether information obtained from the curves of $\Delta H^\ddagger$ and $\Delta S^\ddagger - \Delta S_0^\ddagger$ is applicable to either isotherm. The only definite point to be observed is that the activation enthalpy is negative in the range 3100 to 5250 atmos. It is difficult to imagine what type of activation mechanism could have a negative activation enthalpy associated with it. It is apparent from the isotherms of $\ln D$ vs *P* that different types of structures must exist at the two temperatures. No attempt will be made to analyze the situation at this time.

It is of interest to note, in Table XVI, that in spite of the radical variations observed in the other variables for this system, the free energy of activation rises continually with pressure as for other systems studied.

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