

is thought that  
 osed of  $S_8$  rings  
 res of  $S_n$  chains  
 of  $\log \eta$  vs.  $1/T$   
 below  $160^\circ$  and  
 ve  $\Delta E_{vis}$  equal to  
 ly. A comparison  
 heat of vaporiza-  
 $S_8$  ring structure  
 e and to an  $S_{36}$   
 atures. The exact  
 $S_8$  is not certain;  
 m mixture of  $S_8$   
 different lengths,  
 so as to give an  
 the experimental

It has previously  
 cles require less  
 ion for activation  
 ecules in a series  
 all flowed in the  
 that they would  
 fraction of the  
 length of the chain  
 that  $\Delta E_{vap}/\Delta E_{vis}$   
 normal paraffins  
 is led to the con-  
 ns were curled  
 ow process. Such  
 Langmuir's con-  
 ed in this way in  
 be thought of as  
 of freedom This  
 rocarbon contains  
 olecules, and the  
 e responsible for  
 n of the liquid are  
 details the reader  
 r.

**Application of the  
 Normal Liquids**

ous behavior and  
 es, liquids may be

exclusively undi-  
 Waals, dipole and

- (a) Relatively small molecules  
 E.g.  $CCl_4$ ,  $O_2$ ,  $Cl_2$ ,  $C_2H_5Br$ , ether, decane,  
 acetone, ethyl acetate, etc.
- (b) Very long chain molecules  
 E.g., Linear polymeric resins, such as poly-  
 styrene, polyisobutylene, polyvinyl  
 esters, etc.  
 Very long chain hydrocarbons, such  
 as some lubricating oils  
 Selenium and  $\mu$ -sulfur  
 Raw rubber

**II. Cohesive forces are directed forces in part**

- (a) Hydrogen bond structure  
 E.g.,  $H_2O$ ,  $NH_3$ , alcohols, sugars, alkaloids,  
 nonhardening resins such as cresol-  
 formaldehyde: in general, any liquid  
 whose molecules have OH or NH  
 groups.
- (b) Covalent bond structure  
 E.g.,  $SiO_2$ ,  $GeO_2$ ,  $B_2O_3$ ,  $P_2O_5$ ,  $BeF_2$  and all  
 silicate, borate and phosphate  
 liquids which are not too basic.  
 Hardening resins such as phenol-for-  
 maldehyde, glycerol-phthalic an-  
 hydride, etc.

**III. Metallic liquids—Molten metals**

**IV. Ionic liquids—Molten salts.**

The applications of the theory thus far have  
 been limited to Group I(a), the so-called normal  
 liquids (and also to liquid metals and  $\mu$ -sulfur).  
 Glass-forming liquids are limited to Groups I(b),  
 II(a) and II(b), and in fact most liquids in these  
 groups do form glasses. Groups III and IV are  
 really subdivisions of Group I, but are classified  
 separately for obvious reasons.

In applying the theory to other than normal  
 liquids three points are of importance:

- (1) What is the structure of the liquid?
- (2) What is the unit of flow?
- (3) What is the energy of vaporization of this  
 unit of flow?

In normal liquids the structure of the liquid is  
 fairly certainly known and the unit of flow is  
 without question the molecule, and furthermore  
 the unit of flow and the unit of vaporization are  
 undoubtedly the same. In other than normal  
 liquids the unit of flow, the unit of vaporization,

and the stoichiometric molecule need not neces-  
 sarily be the same.

For any liquid we have the generalization that  
 the energy of making a molecule-sized hole in  
 the liquid is equal to the energy of vaporization,  
 and that

$$\Delta E_{vap} = \frac{1}{2} \sum_{\text{forces}} \text{energy of all attractive and repulsive forces}$$

$$= \frac{1}{2} \left[ \sum_i E_{1i} (\text{van der Waals}) + \sum_i E_{1i} (\text{dipole}) + \sum_i E_i (\text{structural bonds}) \right], \quad (11)$$

neglecting repulsive forces. When an elementary  
 flow process takes place in a liquid possessing a  
 directed bond structure, not only must a hole  
 be provided, but in addition structural bonds  
 must be broken. It seems probable that the  
 energy of activation for flow in a structural  
 liquid will then be  $\frac{1}{3}$  or  $\frac{1}{4}$  of the energy of vapor-  
 ization due to undirected forces *plus all* of the  
 energy of vaporization due to structural bonds:

$$\Delta E_{vis} = 1/n \Delta E_{vap} (\text{undirected forces}) + \Delta E_{vap} (\text{structural bonds}). \quad (12)$$

In normal liquids the last term is zero. In liquids  
 containing hydrogen bonds (Group II(a)) the  
 two components of the energy of vaporization  
 will be comparable in magnitude since the energy  
 of a hydrogen bond is about 6000 cal. But in  
 Group II(b) liquids the energy of breaking the  
 structural bonds will be practically the whole  
 energy of activation, and van der Waals and  
 dipole attractions can be neglected in com-  
 parison, e.g., liquid  $SiO_2$ .

All this applies, of course, to the actual unit  
 of flow, whatever it may be. The unit (or units)  
 of flow can usually be determined if the structure  
 of the liquid and the strength of all the bonds  
 concerned are known. Flow will take place by  
 all possible units of flow, but chiefly by the most  
 economical one, i.e., the one with the smallest  
 energy of activation. For example in liquid  $SiO_2$   
 the units of flow  $SiO$ ,  $SiO_2$ ,  $SiO_3$ , and  $SiO_4$   
 would all require the breaking of 4 Si—O bonds,  
 while any unit of flow containing two silicon  
 atoms would require the breaking of 6 Si—O  
 bonds. Since the energy of an Si—O bond is  
 100,000 cal., the unit of flow will be  $SiO_2$ , or an  
 appropriate mixture of all four of the groups