TABLE II. *Computation of viscosity of $CCl_4$.*

| | | | | | $n=2$ | | $n=3$ | | $n=4$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| $t°C$ | $T°K$ | $V$ cc/MOLE | $\Delta E_{vap}$ KCAL./MOLE | $\eta$(OBS.) MILLI-POISES | $\eta$(CALC.) MILLI-POISES | $\eta$(CALC.)/$\eta$(OBS.) | $\eta$(CALC.) MILLI-POISES | $\eta$(CALC.)/$\eta$(OBS.) | $\eta$(CALC.) MILLI-POISES | $\eta$(CALC.)/$\eta$(OBS.) |
| 0 | 273.1 | 94.3 | 7.56 | 13.47 | 413 | 30.7 | 40.3 | 2.99 | 12.7 | 0.95 |
| 10 | 283.1 | 95.4 | 7.43 | 11.33 | 305 | 26.9 | 33.8 | 2.98 | 11.3 | 1.01 |
| 20 | 293.1 | 96.6 | 7.30 | 9.69 | 232 | 24.0 | 28.8 | 2.98 | 10.1 | 1.04 |
| 30 | 303.1 | 97.8 | 7.18 | 8.42 | 182 | 21.6 | 24.8 | 2.95 | 9.2 | 1.08 |
| 40 | 313.1 | 99.0 | 7.06 | 7.38 | 145 | 19.7 | 21.7 | 2.94 | 8.5 | 1.13 |
| 50 | 323.1 | 100.3 | 6.93 | 6.53 | 115 | 17.6 | 19.1 | 2.92 | 7.8 | 1.19 |
| 60 | 333.1 | 101.6 | 6.81 | 5.84 | 96 | 16.4 | 17.1 | 2.93 | 7.3 | 1.24 |
| 70 | 343.1 | 103.0 | 6.68 | 5.24 | 78 | 14.9 | 15.3 | 2.92 | 6.7 | 1.28 |
| 80 | 353.1 | 104.4 | 6.56 | 4.68 | 66 | 14.2 | 13.8 | 2.95 | 6.4 | 1.36 |

energy of vaporization for such a wide variety of molecules is an interesting fact.

It will be noted that while the plot with $n=4$ in Fig. 3 is parallel to the observed, indicating the correct temperature coefficient, the two plots do not coincide. Viscosities calculated by Eq. (4) are always higher than the observed and the antilogarithm of the difference in ordinate of the parallel plots is the factor by which the calculated values are too large. For all $n=4$ liquids the calculated values are too large by a factor very nearly 2, while the $n=3$ liquids are too large by a somewhat larger and more variable factor varying from 2.5 to 3.5.

One possible explanation of this discrepancy may be that a flowing molecule may possess a "persistence of velocity" and when it has once acquired the necessary activation energy it may move more than one intermolecular distance, and $\lambda$ may be equal to $\lambda_2$, $2\lambda_2$, $3\lambda_2$, etc. for any individual elementary process. It would only be necessary for $\lambda$ to equal $2\lambda_2$ in 40 percent of the elementary processes to give a calculated viscosity too large by a factor of 2, or in 70 percent of the processes for a factor of 3.

Another possible explanation is that the flow process is very likely a bimolecular process rather than a unimolecular one. According to this mechanism two molecules in adjacent layers, which are moving relative to one another, rotate through an angle of about 90° as shown in Fig. 4.[5] The relative motion of successive layers in the liquid is the resultant of many such rotations of pairs of molecules. During the rotation the two molecules will sweep out a volume $\Delta V$, which is the extra volume necessary for the elementary

process to take place, and is obviously $V/3$ and $V/4$ for the two classes of molecules.

The fact that the factors by which the calculated values are too large are about the same for all liquids, and the success of the theory in interpreting the temperature coefficient of vis-
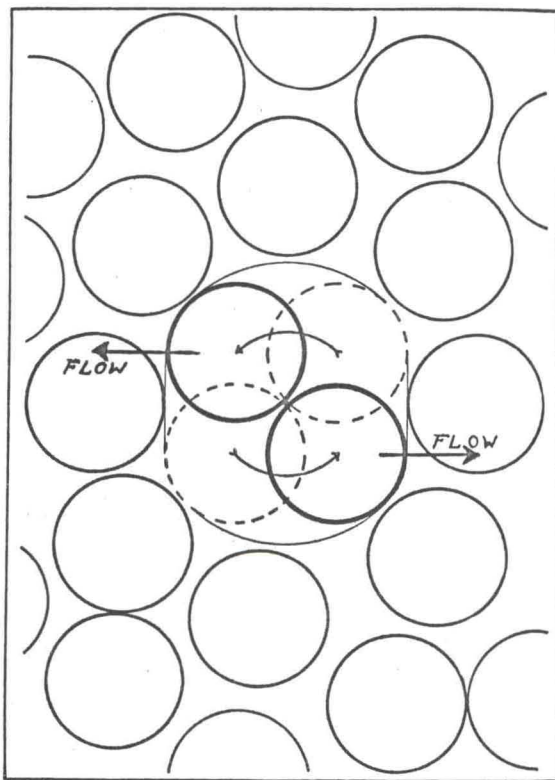


FIG. 4. Bimolecular mechanism of flow.*

* After Hirschfelder, Stevenson and Eyring, J. Chem. Phys. 5, 907 (1937).