CHEMISTRY LETTERS, pp. 65-66, 1972. Published by the Chemical Society of Japan

ON THE DENSITY OF THE LIQUID OF SATURATED HYDROCARBONS. I. A PRELIMINARY MONTE CARLO CALCULATION OF A SQUARE LATTICE MODEL FOR PENTANES.

Keiko KAWASAKI and Haruo HOSOYA[1)]
Department of Chemistry, Ochanomizu University, Bunkyo-ku, Tokyo

A Monte Carlo calculation was performed to obtain the densities of the liquid states of pentanes based on a square lattice model. For the pentane isomers the numbers of the molecules admitted in the lattice are normal>iso>neo in agreement with the observed densities.

The density in a liquid state of a given molecule is determined by the delicate balance of the intermolecular forces, intramolecular rotations and thermal motions of molecules. Close inspection of the collection of the thermochemical data reveals that the difference in the densities of saturated hydrocarbons might be explained fairly well, if not quantitatively, by non-specific geometrical packing of the molecules. However, if a molecule bears no functional group to have any specific interaction, e.g. hydrogen bonding and charge-transfer interaction, with others, relative positions of the neighboring molecules are rapidly changing, as does the form of a molecule among possible rotational isomers. This is just the reason why prediction of several physical and thermochemical properties is far beyond the reach of quantum mechanical calculations as they stand. A Monte Carlo calculation is suitable for this problem.

In order to test our "packing" postulate, first, we have constructed a very crude two-dimensional square lattice model of liquid. "Snap-shots"of the liquid state were taken by using a random-number-generating function in a computer. The assumption and procedures are as follows: i) Assume that the carbon atoms of a saturated hydrocarbon are allowed to occupy only the lattice points specified. Hydrogen atoms are ignored. ii) Give all the lattice points the value 0, meaning vacancy. iii) Choose a point and give it the integer 1, meaning one of the terminal carbon atoms of a given molecule. iv) Choose one of the four neighboring points and give it the integer 2, meaning the second carbon atom. v) Choose one of the three vacant neighboring points and give it the integer 3. vi) This process can be repeated until all the carbon atoms of the molecule are assigned. For a branched molecule the way of the numbering should be defined beforehand. vii) Give all the points adjacent to the carbon skeleton the integer -1, meaning the repulsive region of the van der Waals force. viii) Repeat the steps iii)-vii). If a random number picks up a point whose value is other than 0, go back to the previous step and count one "intra-error". If the number of "intra-error" reaches ten, then give up that molecule, go back to the step iii) and count one "inter-error". ix) If the number of "inter-error" goes up to a threshold value, count the number of the molecule admitted and print out the lattice diagram.

Owing to the size of the available computer[2], 90×90 points were used for the calculation. A practically useful threshold was found to be several hundreds. Fluctuation of the number of a given molecule admitted in different runs was found to be less than 3 per cent. This number can be diminished by a factor of $1/\sqrt{n}$ with the number of experiments n.

Figs.1-3 give parts of the computer output for the three isomers of pentane, where dots represent carbon atoms. The numbers (N) of the admitted molecules are compared with the observed density data in Table I. The threshold value is 500 and each of the calculated numbers is the average of three runs.

Although in this calculation there is no point in estimating the absolute values of the density. the qualitative agreement of the calculated and observed values is meaningful.[3] Several trial calculations on hexanes and heptanes show that this method gives larger numbers for "long molecules". The reasons are clear. As suggested from Fig.1 for n-pentane, unusually bent molecules, like a hair-pin, are allowed in this calculation. Further studies are in progress by a larger computer using three-dimensional multi-entangled diamond lattices.

Footnotes

1) To whom all the correspondence should be addressed.

2) An Okitac-7000 model with 16k memories located in Ochanomizu University.

3) The observed values were taken from the API Report, Project 44, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons"(1945).

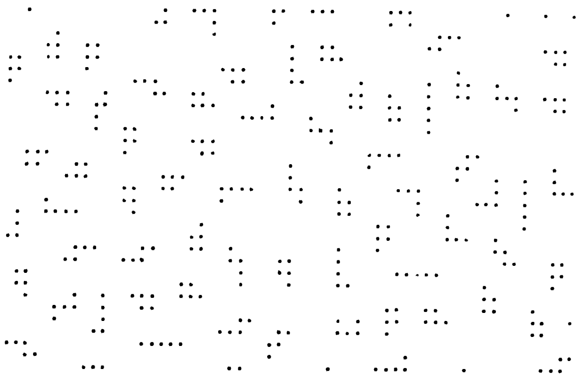


Fig.1. Normal pentane

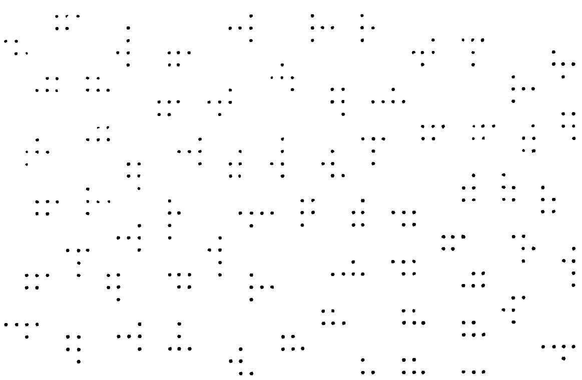


Fig.2. Isopentane

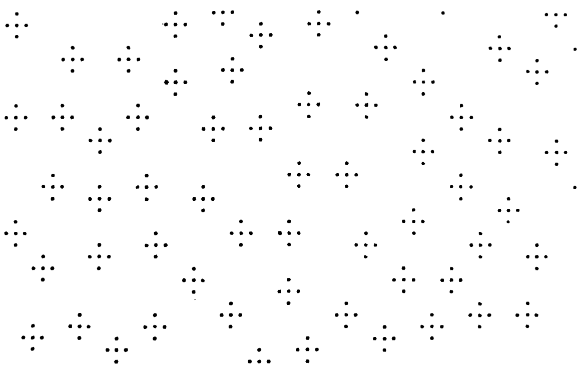
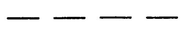
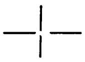


Fig.3. Neopentane

Table I.

Isomer	N	d(g/cm^3)
	321	0.626
	314	0.620
	272	0.591

(Received October 23, 1971)