

## Calculation of the Energy of Vaporization of Perfluorocyclopentane from Intermolecular Forces

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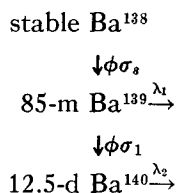
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derive the necessary equation by our procedure. The sequence of transformations was



where the notation is self-explanatory.

The activity of  $\text{Ba}^{140}$  after bombardment of  $\text{Ba}^{138}$  in a flux  $\phi$  for a time  $\tau$  can be calculated as follows. Let  $M$  be the number of  $\text{Ba}^{138}$  nuclei bombarded. Then the rate of formation of  $\text{Ba}^{139}$  is

$$r = \phi \sigma_s M.$$

Using Eq. (II.4) with  $n=2$ , and a "parent decay constant"  $\phi \sigma_1$ , we have for the  $\text{Ba}^{140}$  activity  $A_2(\tau)$ ,

$$A_2(\tau) = \phi \sigma_s M \frac{\lambda_2(\phi \sigma_1)}{\Lambda_2 \Lambda_1 (\Lambda_2 - \Lambda_1)} \times [\Lambda_2(1 - e^{-\Lambda_1 \tau}) - \Lambda_1(1 - e^{-\Lambda_2 \tau})].$$

Now,  $\Lambda_1 \gg \Lambda_2$ , and the circumstances of the experiment were such that  $\tau$  was large, and  $\lambda_2 \gg \phi \sigma_2$ ,  $\lambda_1 \gg \phi \sigma_1$ . Under these circumstances, the above equation becomes

$$A_2(\tau) = \frac{\phi^2 \sigma_s \sigma_1 M}{\lambda_1} (1 - e^{-\lambda_2 \tau}).$$

## Calculation of the Energy of Vaporization of Perfluorocyclopentane from Intermolecular Forces

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By assuming a probable representative orientation of perfluorocyclopentane molecules in the liquid state, the energy of vaporization has been calculated, using both the London-Margenau equation of dispersion forces and the Slater-Kirkwood formula. Using only the data from density and dispersion measurements, fair agreement was found to the value experimentally determined. It is seen on the basis of this calculation that the contribution of the dipole-quadrupole interaction to the London formula is important.

THE extremely low dispersion of the perfluoropentanes as described in a previous paper<sup>1</sup> is one of the types of evidence indicating very small intermolecular forces in fluorocarbons. Of these compounds, perfluorocyclopentane, because of its symmetrical structure, lends itself more easily to theoretical treatment than either the linear or branched chain molecules. On this account this substance has been chosen as a material whose experimental energy of vaporization could be compared with that calculated using existing theories of intermolecular attraction and the physical constants determined in these laboratories.

The molar energy of vaporization  $U$  of a liquid represents the energy required to separate all the molecules of a gram mole of that liquid. If we let  $\sum V_i$  be the total attractive energy between a given molecule and all of its neighbors, then the molar energy of vaporization would be given by the relation

$$U = -\frac{1}{2} N \sum_{i=1}^N V_i, \quad (1)$$

<sup>1</sup> G. H. Rohrbach and G. H. Cady, J. Am. Chem. Soc., to be published.

where  $N$  is Avogadro's number and  $\frac{1}{2}$  is included to avoid counting each bond twice. Equation (1) assumes, of course, that the force acting on every molecule is the same, which cannot be the case for the surface molecules. However, for any large number of molecules being considered, this factor may be neglected. This equation further neglects the small configurational energy of the vapor and also assumes that there is no difference between the kinetic energies in the liquid and vapor phases.

Attraction between the non-polar molecules of perfluorocyclopentane must be due entirely to van der Waals forces of the dispersion type. As a first approximation these forces are known to be proportional to the inverse 6th power of the distance  $R$ , such a relation for the attraction between two spherical atoms being first derived by London.<sup>2</sup> It is generally recognized at present that there is attractive contribution from still higher inverse terms, and a better representation for the attractive potential is given by<sup>3</sup>

$$V = -C_1/R^6 - C_2/R^8 - C_3/R^{10}, \quad (2)$$

<sup>2</sup> F. London, Zeits. f. physik. Chemie B11, 222 (1930).

<sup>3</sup> H. Margenau, Rev. Mod. Phys. 11, 1 (1939). This paper is an excellent review of the theories of intermolecular forces

TABLE I.

Distance between molecular centers	No. of pairs of centers	$\Sigma 1/R^6$ (cm <sup>-6</sup> )	$\Sigma 1/R^8$ (cm <sup>-8</sup> )
7.07Å	300	$4.25 \times 10^{45}$	$1.41 \times 10^{60}$
10.0Å	150	$0.207 \times 10^{45}$	$0.01 \times 10^{60}$
12.24Å	100*	$0.102 \times 10^{45}$	$0.01 \times 10^{60}$
Total	550	$4.56 \times 10^{45}$	$1.43 \times 10^{60}$

\* Only the terms with  $R < 11\text{Å}$  were considered. In all there are 600 pairs for this distance between centers, but the larger  $R$  values made negligible contribution.

where the constants  $C_1$ ,  $C_2$  and  $C_3$  are all temperature independent. Just what contribution is made by each term cannot be stated simply. Certainly the first, London's dipole-dipole interaction, is dominant, although at small distances the others may become important. For example, by deriving an expression to account for the dipole-quadrupole interaction ( $-C_2/R^8$ ), Margenau<sup>4</sup> has shown that the calculated potential attraction for hydrogen and helium is increased 25–50 percent. Again Spomer and Bruch-Willstatter<sup>5</sup> in the calculation of the sublimation energy of solid CO<sub>2</sub> found that the second term amounted to 52–56 percent of the first.

In addition to the attractive forces there exist at small distances repulsive forces which are very nearly represented by a term proportional to the inverse 12th power. These repulsive forces would tend to cancel in part some of the contribution of the higher terms of attraction.

For the purpose of the calculations for perfluorocyclopentane two different formulae will be used. The first is Margenau's<sup>4</sup> second approximation to London's dispersion formula, which includes the dipole-quadrupole energy contribution:

$$V = -\frac{3}{4} h \nu_0 \alpha^2 \left[ \sum_i 1/R_i^6 + (9\alpha h \nu_0 / 2e^2) \sum_i 1/R_i^8 \right]. \quad (3)$$

In this equation the factor  $e$  is the elementary electron charge,  $h$  is Planck's constant,  $\alpha$  is the polarizability, and  $\nu_0$  is London's zero-point frequency. The attractive term of still higher power and the repulsive term are considered to have canceling contribution and are neglected.

Slater and Kirkwood<sup>6</sup> have derived another formula by a different method in which the molar binding energy of non-polar atoms is given by

$$U = 1.63 \times 10^{-10} n^{\frac{1}{2}} \alpha^{\frac{1}{2}} \sum_i 1/R_i^6 \text{ (kcal./mole)}, \quad (4)$$

where  $n$  is the number of electrons in the valence

with a discussion of the importance of the various terms. The first term ( $-C_1/R^6$ ) is the "dipole-dipole" interaction of London, the second ( $-C_2/R^8$ ) is the "dipole-quadrupole" contribution, while the third ( $-C_3/R^{10}$ ) is due to the "quadrupole-quadrupole" interaction.

<sup>4</sup> H. Margenau, Phys. Rev. **38**, 747 (1931).

<sup>5</sup> H. Spomer and M. Bruch-Willstatter, J. Chem. Phys. **5**, 745 (1937).

<sup>6</sup> J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

shell of the atoms. If it is to be applied to the case where more than one atom constitutes the attracting center,  $n$  is taken as equal to the total number of valence electrons. Again the factor  $\alpha$  is the polarizability of the attracting center.

Although this latter relation does not include a term for dipole-quadrupole interaction (which still should be added), it is probable that this is not as important as with the London formula. This is apparent since the results from the Slater-Kirkwood formula are consistently higher than those from the simple London equation. Indeed, as Spomer and Bruch-Willstatter point out, if recent calculations of Page<sup>7</sup> on helium are capable of generalization, the result of the Slater-Kirkwood formula would be the same as that of London's equation with Margenau's second approximation included. In the calculation of the sublimation energy of solid benzene, deBoer<sup>8</sup> obtained satisfactory results using the single term of the Slater-Kirkwood approximation.

The factor  $\alpha$  in the two dispersion formulas represents the polarizability of the attracting center, and it is obtainable from the well known relation:

$$4/3\pi N\alpha = [(n_\infty^2 - 1)/(n_\infty^2 + 2)](M/\rho) = P_E + P_A. \quad (5)$$

Here  $n_\infty$  is the refractive index at infinite wavelength,  $N$  is Avogadro's number, while  $M$  and  $\rho$  represent the molecular weight and density, respectively. To obtain directly the desired value of  $\alpha$  it is necessary to measure the refractive index in the infra-red, since extrapolation from the visible region only gives the contribution of the electron polarization ( $P_E$ ). However, for most substances the additional atomic polarization term ( $P_A$ ) is small, about 3 cc, and as a fair approximation the extrapolated value may be increased by this amount. In the case of perfluorocyclopentane the extrapolation to infinite wave-length gives  $P_E = 24.3$  cc; then if we include 3 cc for the polarization contribution due to nuclear displacement, we obtain

$$\alpha = 1.08 \times 10^{-23} \text{ cc.}$$

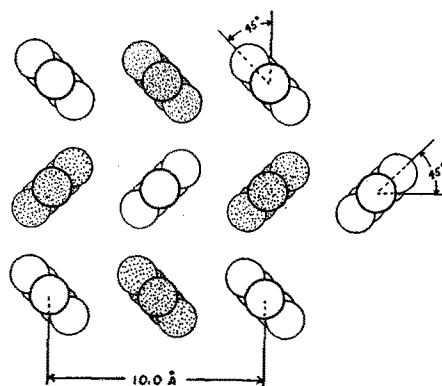


FIG. 1.

<sup>7</sup> C. H. Page, Phys. Rev. **51**, 1002 (1937).

<sup>8</sup> J. H. deBoer, Trans. Faraday Soc. **32**, 10 (1936).

The refractive index of a medium varies with the wave-length of the light according to the form

$$n = 1 + \sum_i (a_i / (\nu_0^2 - \nu^2)), \quad (6)$$

as has been derived in the classical electromagnetic theory and confirmed by quantum theory. In Eq. (6)  $n$  is the refractive index measured with light of frequency  $\nu$ ,  $a$  is a constant in each term of the series, and  $\nu_0$  is the same characteristic frequency as found in the London dispersion equation. Using the simple form of only one term of the summation, from the dispersion data\* of perfluorocyclopentane we have for the characteristic frequency:

$$\nu_0 = 4.87 \times 10^{15} \text{ sec.}^{-1}.$$

The first calculation of the energy of vaporization is made considering the intermolecular forces to originate from the centers of the molecules. From density measurements at 15°C ( $\rho = 1.6610$ ),<sup>9</sup> assuming a close-packed cubic face centered orientation (which is probably very nearly the case with molecules of this shape), the distances to the two nearest sets of surrounding molecules are calculated (12 molecules at  $R = 7.07\text{\AA}$ ; 6 molecules at  $R = 10.0\text{\AA}$ ). Neglecting any anisotropy of the polarizability, application of the two formulas gives:

London ( $R^{-6}$  term only):  $U = 2.1 \text{ kcal./mole}$ ,  
Slater and Kirkwood:  $U = 2.8 \text{ kcal./mole}$ .

These are considerably lower than the value measured by Barber,<sup>10</sup> who gives the energy of vaporization at constant volume for 15°C as equal to 5.80 kcal./mole. Inclusion of the inverse 8th term in the London formula increases the energy value to very nearly 3 kcal./mole.

The second calculation is made by considering each  $\text{CF}_2$  group as an attracting center for the similar groups in the other molecules. This procedure should provide a more reasonable basis for calculation than does the assumption of a single attracting center for each molecule, since the peripheral atoms approach each other much more closely than do the molecular centers. Again, a close-packed cubic arrangement for the centers of the molecules is assumed, but in this case it is necessary to assume some instantaneous orientation pattern as well. Actually, the molecules of perfluorocyclopentane are rotating, but in order to calculate the attractive energies between  $\text{CF}_2$  groups we assume an instantaneous orientation having substantially the same total attractive potential as with random orientation. The arrangement chosen

is as pictured in Fig. 1, with the shaded molecules having their centers in a plane either 5.00Å\*\* above or below the plane of the drawing.

The polarizability for the  $\text{CF}_2$  group is now taken as equal to one-fifth the molecular polarizability,

$$\alpha_{\text{CF}_2} = 2.16 \times 10^{-24} \text{ cc},$$

while the characteristic frequency of the five identical subparts is assumed to be that of the entire molecule; thus

$$\nu_{0\text{CF}_2} = 4.87 \times 10^{15} \text{ sec.}^{-1}.$$

The anisotropy of the polarizability is again neglected, but, by reason of the assumed relative positions of the molecules, it is felt that this neglect is not serious. It is recognized, of course, that the polarizability of the  $\text{CF}_2$  centers is not spherical but that it probably does not have an anisotropy very much greater than 2:1. Because the value used is an average one between the three component directions and because the pairing occurs between a large number of separate groups with varying orientations, the anisotropic effects should tend to balance out.

Using the bond distance  $\text{C}-\text{C} = 1.45\text{\AA}$ <sup>11</sup> and  $\text{C}-\text{F} = 1.35\text{\AA}$ <sup>12</sup> with a tetrahedral angle between the two fluorine atoms on each carbon, the positions of the five centers can be calculated. They are located not at the centers of the carbon atoms, but at a distance 0.51Å farther out corresponding to the center of electron density. Each center is located by finding the center of gravity of three negative charges 3, 7, 7 assumed to exist at the centers of the carbon and two fluorine atoms, respectively.

Rather than calculate all the possible distances, metal pentagons were carefully machined to scale ( $1\text{\AA} = 1 \text{ inch}$ ) and set up in the various positions according to the orientation model. Distances were then measured by calipers and read to the nearest 0.01 inch. The summation of the reciprocal 6th and 8th powers of the distances are given in Table I. Using the values from the 3rd and 4th columns of the above table, application of the formulas gives

London ( $R^{-6}$ term only):	3.7 kcal./mole,
London and Margenau:	5.3 kcal./mole,
Slater and Kirkwood:	5.1 kcal./mole,

this time in much better agreement with the measured value of 5.80 kcal./mole.

#### ACKNOWLEDGMENT

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\*\* Using density value  $\rho = 1.6610$ .

<sup>11</sup> E. L. Pace, J. Chem. Phys. 16, 74 (1948). ( $\text{C}-\text{C}$  distance in  $\text{C}_2\text{F}_6$ .)

<sup>12</sup> L. O. Brockway, J. Phys. Chem. 41, 185 (1937).

\* The determined values of refractive index at 15°C are:

$H_2 \cdots (6563\text{\AA}); n = 1.2576;$

$H_F \cdots (4861\text{\AA}); n = 1.2595.$

<sup>9</sup> L. L. Burger, Thesis, University of Washington (1948).

<sup>10</sup> E. J. Barber, Thesis, University of Washington (in preparation).