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Citation: *J. Chem. Phys.* **12**, 321 (1944); doi: 10.1063/1.1723948

View online: <http://dx.doi.org/10.1063/1.1723948>

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### Surface Tension and van der Waals' Equation

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May 29, 1944

IN recent years the theory of the liquid state has attracted considerable attention and several models have been proposed with the object of deriving the essential properties of liquids by applying the methods of statistical mechanics. The model which is of interest to us here is that of Fürth,<sup>1</sup> in which the liquid is assumed to be a continuum permeated with holes. The number of holes is taken to be equal to the number of molecules in the liquid. This picture of a liquid is just the reverse of the picture of a gas in the kinetic theory, for in the former case almost empty holes are supposed to move in a continuous material medium whereas in the latter case material particles move in empty space. The holes contain vapor at the vapor pressure corresponding to the temperature of the liquid.

The size of a hole in Fürth's treatment is not treated as fixed, but the hole can expand and contract and the probability distribution of the size is determined by an application of Boltzmann's law in the usual manner.

Fürth's theory easily leads to an expression for the intrinsic pressure  $p_0$  in the liquid<sup>2</sup>

$$p_0 = 1.3[\sigma^3/(kT)^{\frac{1}{2}}], \quad (1)$$

where  $k$  is the Boltzmann constant,  $T$  the absolute temperature, and  $\sigma$  the surface tension at that temperature.

TABLE I.

Substance	$p_0$ in atmos.	$a_2^*$	Substance	$p_0$ in atmos.	$a_2$
K	$50 \times 10^3$	$31 \times 10^{-2}$	H <sub>2</sub>	$0.15 \times 10^3$	$0.022 \times 10^{-2}$
Na	29	5.8	A <sub>1</sub>	0.59	0.22
Hg	81	5.2	Ne	0.29	0.030
Zn	89	3.7	CCl <sub>4</sub>	1.2	8.0
Sn	57	7.3	CS <sub>2</sub>	2.6	4.2
Cd	66	5.8	C <sub>6</sub> H <sub>6</sub>	1.1	5.8
Pb	41	8.8	C <sub>6</sub> H <sub>12</sub>	0.97	8.0
Tl	36	6.7	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	2.1	9.9
P <sub>4</sub>	2.3	7.7	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	1.9	12
S <sub>8</sub>	2.5	3.5	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> NH <sub>2</sub>	1.4	9.9
Se <sub>2</sub>	4.5	4.0	C <sub>10</sub> H <sub>8</sub>	1.1	9.7
Br <sub>2</sub>	2.0	3.6	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NH	1.4	20
N <sub>2</sub>	0.56	0.25	(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub>	1.1	28
O <sub>2</sub>	1.5	0.32			

\* The unit of pressure is the standard atmosphere and the unit of volume the gram molecular volume of an ideal gas at N.T.P.

The value of the internal pressure for various substances at their melting points (strictly triple points) as given by Eq. (1) is given below. The values for the surface tension have been taken from Fürth's paper (see Table I).

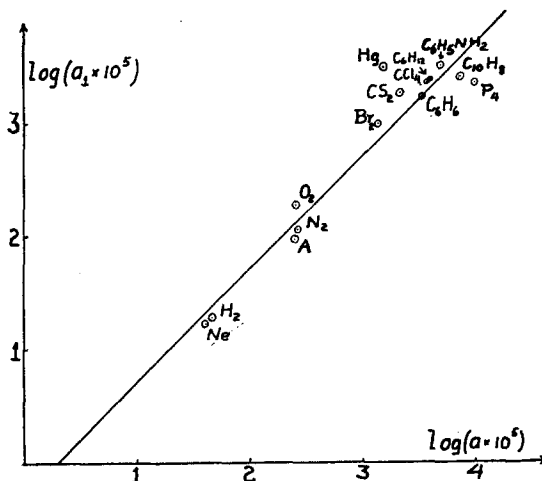


FIG. 1. The abscissae denote the experimental values for van der Waals' constant  $a$  and the ordinates the values  $a_1$  obtained from Fürth's theory.

As is well known, the internal pressure  $p_0$  in a liquid is defined as

$$T(\partial p_0/\partial T)_V = T\alpha/\beta, \quad (2)$$

where  $\alpha$  is the coefficient of expansion and  $\beta$  is the coefficient of compressibility. If van der Waals' equation be assumed to apply to a liquid, the internal pressure is given by  $a/V^2$  where  $V$  is the molecular volume and  $a$  is the molecular force term in van der Waals' equation. Thus we have

$$p_0 = a/V^2, \quad (3)$$

and from this it is easily shown that the internal pressure is also equal to the latent heat of vaporization at constant volume per unit volume. The hole theory of the liquid state leads immediately to a connection between van der Waals'  $a$  and surface tension  $\sigma$ . This relation is of interest for it was through his studies of surface tension that van der Waals was led to the equation of state. From (1) and (3) we obtain for the van der Waals' force constant

$$a_1 = 1.3V^2[\sigma^3/(kT)^{\frac{1}{2}}]. \quad (4)$$

It is to be noted that as  $\sigma$  decreases with increasing temperature the value  $a_1$  will decrease with increasing temperature. This is in accordance with observation. In Fig. 1  $\log(10^5 a_1)$  is plotted against  $\log(10^5 a)$ ,  $a_1$  being calculated from the above relation. (The values of  $a$  have been taken from *Handbook of Chemistry and Physics*.<sup>3</sup>) It will be observed from Fig. 1 that  $a$  is proportional to  $a_1$  and the constant of proportionality is nearly 2.0, whereas the theory requires it to be unity. However, considering the approximate nature of Fürth's model this discrepancy cannot be considered unreasonable.

In a paper to be published shortly we have constructed and solved the Schrödinger equation for a hole in a liquid and determined the eigenvalues of its energy. On this theory we are led to an expression for the intrinsic pressure which does not contain the temperature but only the surface tension and density of the liquid. This gives for the intrinsic pressure the value

$$p_0 = 3.5\sigma(7\pi\sigma/15E)^{1/2},$$

and for the van der Waals' force constant the value

$$a_2 = 3.5\sigma V^2(7\pi\sigma/15E)^{1/2}, \quad (5)$$

where  $E = 3.1h^{4/7}\sigma^{5/7}/\rho^{2/7}$ ,  $h$  being the Planck constant. In Fig. 2  $\log(10^5 a_2)$  has been plotted against  $\log(10^5 a)$  and

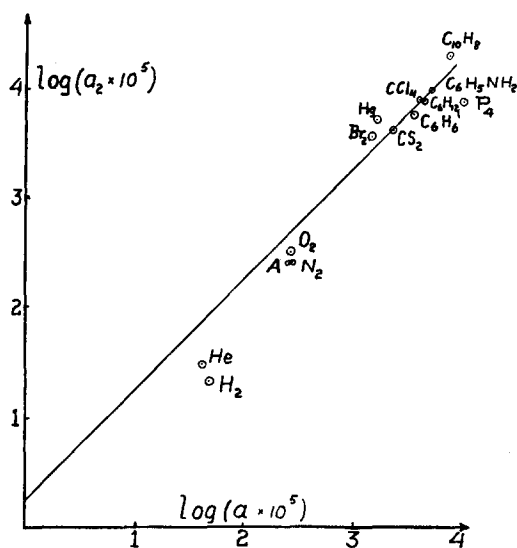


FIG. 2. The abscissae denote the experimental values for van der Waals' constant  $a$  and the ordinates the values of  $a_2$  obtained from Eq. (5).

the agreement is satisfactory. The constant of proportionality is again 0.6 instead of being unity.

In the paper referred to above various other applications of the modified hole theory have been discussed, but it is interesting to find that the hole theory leads immediately to a relation between surface tension and van der Waals' constant.

We are very grateful to Dr. Kothari for his kind interest in the work.

<sup>1</sup> Fürth, Proc. Camb. Phil. Soc. **37**, 252 (1941).

<sup>2</sup> See also R. S. Silver, Nature **150**, 605 (1942). It is interesting to note that water passes up through the conduit of trees in a state of tension [Dixon, Proc. Roy. Soc. **B125**, 1 (1938)].

<sup>3</sup> Handbook of Chemistry and Physics (Chemical Rubber Publishing Company, Cleveland, 1937-1938), 22nd edition.

## Copolymerization of Systems of Three and More Components

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May 2, 1944

IN a recent paper<sup>1</sup> these authors have shown that with a steady state assumption the course of copolymerization of a system of two components can be calculated without restricting assumptions as to the relative values of the rate constants involved.

Similarly it is possible to calculate the course of copolymerization of a system of any number of components. This, however, is rather involved because of the great number of rate constants which must be considered. Even the answer to the limited question of the polymer as a function of monomer composition involves  $x(x-1)$  rate constant ratios (where  $x$  is the number of components). Thus, for a system of three components,  $A$ ,  $B$ , and  $C$ , where nine rates of growths are involved, six ratios are required; namely,

$$\alpha^b = k_2^{ab}/k_2^{aa}; \quad \alpha^c = k_2^{ac}/k_2^{aa}; \quad \beta^a = k_2^{ba}/k_2^{bb};$$

$$\beta^c = k_2^{bc}/k_2^{bb}; \quad \gamma^a = k_2^{ca}/k_2^{cc}; \quad \gamma^b = k_2^{cb}/k_2^{cc},$$

where the first upper index denotes the nature of the active group in which the growing chain ends and the second upper index the monomer added in the process. Then the initial polymer composition  $a/b/c$  is:

$$\frac{a}{b} = \frac{\beta^a \gamma^b AB + \gamma^a A(\beta^a A + \beta^c C)}{\alpha^b \gamma^a AB + \gamma^b B(\alpha^b B + \alpha^c C)} \cdot \frac{A + \alpha^b B + \alpha^c C}{B + \beta^a A + \beta^c C} \quad (1)$$

$$\frac{a}{c} = \frac{\beta^a \gamma^b AB + \gamma^a A(\beta^a A + \beta^c C)}{\alpha^c \beta^a AC + \beta^c C(\alpha^b B + \alpha^c C)} \cdot \frac{A + \alpha^b B + \alpha^c C}{C + \gamma^a A + \gamma^b B} \quad (2)$$

Equations (1) and (2) indicate the possibility of predicting the composition of a multipolymer from information gathered from a separate study of each pair of monomers involved. The knowledge of the ratios of the propagation rate constants for each pair of monomers also permits the calculation of the size distribution curve of sequences of units of one kind. This is worth-while information which, in most cases, cannot be obtained otherwise. Thus if the monomer mixture is made up of the monomers  $A$ ,  $B$ ,  $C$ ,  $\dots$ ,  $Y$ , the resulting initial copolymer will consist of sequences of  $a$ ,  $b$ ,  $\dots$  and  $y$  monomer units. The fraction of all  $a$  sequences which possess  $n_a$  monomer units will be given by a distribution function  $N(n_a)$ .

$$N(n_a) = \left( \frac{A}{A + \alpha^b B + \alpha^c C + \dots + \alpha^y Y} \right)^{(n-1)} \times \left( 1 - \frac{A}{A + \alpha^b B + \alpha^c C + \dots + \alpha^y Y} \right) \quad (3)$$

In many cases of interest the  $a$  sequences will consist mainly of one member—i.e., isolated  $a$  units. In other cases relatively long sequences of  $a$ 's will be present in the copolymer.

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<sup>1</sup> T. Alfrey and G. Goldfinger, J. Chem. Phys. **12**, 205 (1944).