On the Catalyst Surface Structure

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cluster, provided that the volume fraction of polymer segments is everywhere small.[4] Higher virial coefficients may, in principle, be calculated from the phase integral over the product of factors $[1-f(a_{ij})]$.[5] Straightforward evaluation of these integrals would be hopelessly laborious, but approximate evaluation in the "equivalent sphere" approximation gives[6]

$$C' = (5/8)(B')^2. \tag{10}$$

The parameters C_1 and κ_1 (which is inversely proportional to temperature) are indicative of the magnitudes of the entropy and heat of mixing of polymer segments with solvent. Their evaluation from B' (and C') and its temperature coefficient is complicated by the occurrence of the intramolecular expansion factor α in β' and K. This factor also is dependent on temperature.[1, 7] It would appear that the elucidation of the fundamental parameters governing polymer-solvent interaction in dilute solutions may best be achieved through a combination of osmotic and viscosity measurements (or some other measure of molecular dimensions, e.g., angular dissymmetry of scattered light) on the same system at different temperatures. Contrary to the usual assumptions, π/c should not vary linearly with c in dilute solutions and the limiting slope is not independent of M. The same conclusions were reached previously.[2]

As $\kappa_1 \to \frac{1}{2}$, Eq. (9') simplifies through virtual disappearance of higher terms in the series. At $\kappa_1 = \frac{1}{2}$, which corresponds to incipient limited miscibility for infinite molecular weight, the excluded volume becomes zero, the second and higher virial coefficients vanish, and Eq. (1) reduces to Van't Hoff's law, as has been found experimentally for polyisobutylene in benzene one degree above the critical temperature for total miscibility.[8] The disappearance of the resistance to overlapping of the molecules as κ_1 approaches $\frac{1}{2}$ provides an explanation for the enhanced dependence of η_{sp}/c on concentration in poor solvents.

[1] P. J. Flory, J. Chem. Phys. 17, 303 (1949).
[2] P. J. Flory, J. Chem. Phys. 13, 453 (1945).
[3] The notation follows closely that used in reference (1), except for the replacement of μ_1 by κ_1.
[4] Otherwise, approximations used in deriving Eq. (3) no longer are valid.
[5] See J. G. Kirkwood, J. Chem. Phys. 3, 300 (1935).
[6] L. Boltzmann, *Vorlesungen uber Gastheorie* (Verlag Abschnitt, Leipzig, 1898), Vol. II, p. 138.
[7] T. G. Fox, Jr., and P. J. Flory, J. Phys. Coll. Chem. 53, 197 (1949).
[8] P. J. Flory, J. Am. Chem. Soc. 65, 372 (1943).

Microwave Investigations of Chloroform*

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October 3, 1949

THE $J=2$ to 3 and $J=3$ to 4 rotational transitions of $CHCl_3{}^{35}$ have been observed by the techniques of Stark modulation[1] using a coiled cell of twenty-four foot equivalent length, and a four kilocycle modulation frequency. Since each chlorine nucleus gives rise to a quadrupole splitting of the energy levels,[2] the resolved structure is rather complex, and the individual lines are weak. At pressures near one millimeter of mercury however, the strongest lines of $CHCl_3{}^{35}$ integrate to form a single absorption peak about 28 megacycles wide centering at 26,417 megacycles for the $J=3$ to 4 transition. The corresponding moment of inertia I_B is 254.1 $\times 10^{-40}$ g cm^2.

For $CHCl_3$, 96 percent of I_B is contributed by the chlorine atoms, and about two percent each by the carbon and hydrogen. The structure thus is insensitive to isotope variation, although information from $CDCl_3$, which we are endeavoring to obtain, would be useful. This insensitivity of structure to isotope however allows rather accurate determination of the C—Cl and, especially, the Cl—Cl distances from a single moment of inertia. If the C—H distance is assumed to be 1.11A (equal to the value for CH_3Cl),[3] a value of the H—C—Cl angle of $106° \pm 3°$ (consistent with electron

diffraction data)[4] gives a Cl—Cl distance of 2.91 ∓ 0.01A, and a C—Cl distance of 1.75 ± 0.02A. These values, while within the limits of electron diffraction data, are somewhat shorter than the average values. The C—Cl bond is shorter than the value of 1.779 found for methyl chloride,[3] a trend similar to that observed with CHF_3 and CH_3F.[5]

[1] R. H. Hughes and E. B. Wilson, Jr., Phys. Rev. 71, 562 (1947).
[2] Townes, Holden, Hardeen, and Merritt, Phys. Rev. 71, 644 (1947).
[3] Gordy, Simmons, and Smith, Phys. Rev. 74, 243 (1948).
[4] Louis R. Maxwell, J. Opt. Soc. Am. 30, 374 (1940).
[5] Gilliam, Edwards, and Gordy, Phys. Rev. 75, 1014 (1949).

On the Catalyst Surface Structure

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October 24, 1949

IN a recent article, Sips[1] advanced a mathematical formulation claiming to have established a method using which the heterogeneity of a catalyst surface can be calculated rigorously from an experimental isotherm. A close examination of his formulation reveals that it is unsatisfactory and in fact it cannot be of much use. While we have not been able to establish a new and useful formulation, we feel that it is important to point out his erroneous approach.

Before going into detail, the notation used by Sips must be corrected. In order to fulfill his condition $\int_{-\infty}^{+\infty} N(q)dq = 1$ $N(q)$ should represent the *fraction* of the number of sites having heat of adsorption q instead of the number itself as designated by Sips. His errors may be summarized as follows:

(1) His Eq. (2) may be rewritten as

$$\theta = \sum_{q=-\infty}^{+\infty} \frac{N(q)}{1+(a/p)\exp(-q/RT)}. \tag{a}$$

After he gets the formulation of $N(q)$ by using the Freundlich isotherm, he is unable to obtain the original isotherm because the integral is "intractable". Without carrying out the integration, we can see from Eq. (a) that the resultant isotherm must be the Langmuir and not the Freundlich type. His treatment therefore fails to give a consistent result.

(2) It is to be noted that no matter what analytical form $N(q)$ may take, Eq. (a) will only yield a Langmuir isotherm. The sigmoidal isotherm which is commonly obtained cannot be possibly described by Sips' isotherm thus indicating the invalidity of the formulation. In fact, if one uses the *BET* isotherm equation in the uncondensed form to evaluate the heterogeneity distribution function, one finds that $N(q)=0$ for all values of q except for $q=-\infty$. This contradicts the original postulates from which $N(q)$ is derived and proves further the treatment lacking of consistency.

(3) Sips claims that the lack of knowledge of the form of the function of an experimental isotherm being "no obstacle, because the experimental values may always be represented as exactly as we like by using analytical expressions." This is fundamentally wrong. The function we need to calculate the distribution function $N(q)$ must not only describe the experimental isotherm well; but also represent the true mechanism, about which we have very little knowledge. Assigning an arbitrary form to the adsorption isotherm equation is equivalent to assigning an arbitrary form to $N(q)$. This will be discussed more fully elsewhere.

(4) Repeatedly, Sips is troubled by the non-convergence of $\int_{-\infty}^{+\infty} N(q)dq$. When working with the Freundlich isotherm, he attributes the reason to the form of the isotherm equation which goes to infinity when $p=\infty$. This is incorrect. The $N(q)$ evaluated by Sips' method should be valid for all the region where the isotherm equation is valid. Plainly, when the integration is carried

out from $q = -\infty$ to $+\infty$, the pressure can still remain low, fulfilling the condition under which the Freundlich isotherm is valid; and $\int_{-\infty}^{+\infty} N(q)dq$ would therefore remain finite if Sips' reasoning were sound. The non-convergence character of $\int_{-\infty}^{+\infty} N(q)dq$ is actually a consequence of Sips' use of Eq. (1) in which he contends that those sites where $q = -\infty$ are not counted. Therefore the lower integration limit of $\int N(q)dq$ should be some finite value instead of being $-\infty$ in order to make the operation consistent. Such a change in limit makes the integral convergent at all pressures where the isotherm equation holds.

In conclusion, Sips' treatment can only be useful if (a) the Langmuir isotherm is valid and (b) the isotherm equation representing the true adsorption mechanism (and not merely an analytical expression giving all the approximately correct *numerical* values) is known. These conditions practically deprive his formulation of all its significance, because the first condition is not always met and the second cannot yet even be approximated. Even if both conditions can be met, the function $N(q)$ obtained does not necessarily satisfy the equation $\int_{-\infty}^{+\infty} N(q)dq = 1$.

[1] R. Sips, J. Chem. Phys. **16**, 490 (1948).

The Triple-Dipole Interaction between Atoms and Cohesion in Crystals of the Rare Gases

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October 3, 1949

THE application of third-order perturbation theory to the interaction of neutral atoms was reported[1] to result in an interaction between triplets of atoms. The term in the third-order interaction energy which depends on triplets of atoms is

$$W_0''' = \sum_{\substack{j \neq 0}} \sum_{\substack{k \neq 0 \\ k \neq j}} \frac{H_{0j}H_{jk}H_{k0}}{(W_j - W_0)(W_k - W_0)}, \tag{1}$$

where W_j, W_k, and W_0 are the unperturbed energies of the intermediate states j and k, and the ground state, respectively. H_{0j} etc. are the matrix elements of the perturbation. If the perturbing potential is limited to the dipole-dipole term, the following approximate expression, called the triple-dipole interaction, is obtained for W_0'''.

$$W_0''' \cong \frac{3}{2} \frac{(V_1 + V_2 + V_3)V_1V_2V_3\alpha_1\alpha_2\alpha_3(3\cos\gamma_1\cos\gamma_2\cos\gamma_3 + 1)}{(V_1 + V_2)(V_2 + V_3)(V_1 + V_3)R_{12}{}^3R_{23}{}^3R_{13}{}^3}. \tag{2}$$

V_1, V_2, and V_3 are the ionization potentials and α_1, α_2, and α_3 the polarizabilities of the three atoms; R_{12}, R_{23}, and R_{13} are the sides and γ_1, γ_2, and γ_3 the angles of the triangle formed by the nuclei of the atoms. For like atoms (2) becomes:[2]

$$W_0''' \cong \frac{9}{16} \frac{V\alpha^3(3\cos\gamma_1\cos\gamma_2\cos\gamma_3 + 1)}{R_{12}{}^3R_{23}{}^3R_{13}{}^3}. \tag{2a}$$

The triple-dipole interaction W_0''' is positive, i.e., repulsive, for all acute triangles and negative for most obtuse triangles.

It can be shown that W_0''' for three rare gas atoms is about one percent of the dipole-dipole interaction energy of the London type.[3] Since W_0''' is relatively small, it does not appear likely to contribute much to the cohesive energy even for molecular crystals. The dependence of W_0''' on the configuration of three atoms, however, suggested that the structure of the rare gas solids might be explained by the triple-dipole interaction. Argon, neon, krypton, and xenon crystallize in the face-centered-cubic lattice, one of the two closest-packed structures,[4] the other being the hexagonal-closest-packed lattice. London[5] showed that, assuming pairwise

additivity, the dipole-dipole interaction accounted largely for the cohesion of molecular crystals. However, the lattice sums of the dipole-dipole interaction for the f.c.c.[6] and h.c.p.[7] lattices do not differ by more than 0.01 percent. This is also true if the dipole-quadrupole or higher pole interactions are similarly summed, so the stability of the f.c.c. compared to the h.c.p. structure cannot be explained by differences in these interactions.

The triple-dipole interaction, W_0''', was directly summed in both the f.c.c. and h.c.p. lattices for a cylindrical region whose radius and semi-altitude were about three times the nearest-neighbor distance. These calculations were made on IBM punched-card machines.[8]

For the above region the sum of W_0'''/K, where K equals $\frac{9}{16}V\alpha^3/r_0{}^9$, is 56.686 for the f.c.c. and 56.727 for the h.c.p. lattice. From an examination of partial sums it seems that: (a) W_0'''/K converges to a value close to 57 and (b) the sum of W_0'''/K is roughly 0.04 greater for the h.c.p. compared to the f.c.c. lattice.

The triple-dipole interaction was computed for crystals of the rare gases using accepted values of V, r_0, and α, and 56.69 for the sum of W_0'''/K. From the results of Table I it is noted that the

TABLE I. Triple-dipole interaction for crystals of rare gases.

Element	Lattice sum of W_0''' (repulsion) kcal./mole	Heat of sublimation kcal./mole
Neon	0.0090	0.51
Argon	0.093	1.86
Krypton	0.229	2.57
Xenon	0.335	3.59

triple-dipole interaction amounts to two to nine percent of the cohesive energy for most rare gas solids.

It seems unlikely that the difference in the triple-dipole interaction for the f.c.c. compared to the h.c.p. lattice, a difference less than a ten-thousandth of the cohesive energy, can explain the stability of the f.c.c. lattice for the rare gas elements. Details of this work will be published later.

[1] B. M. Axilrod and E. Teller, J. Chem. Phys. **11**, 299 (1943).
[2] The equation for W_0''' in reference 1 was incomplete in that the factor $\frac{3}{2}$ had not been determined. In March, 1948, a letter was received from Mr. Yosio Muto of Japan who had also worked out the triple-dipole interaction. Mr. Muto's result for W_0''' appeared to be in agreement with (2a).
[3] The dipole-dipole interaction energy is approximately $-\frac{3}{4}(V\alpha^2/R^6)$ for like atoms.
[4] *Handbook of Chemistry and Physics* (1945).
[5] F. London, Trans. Faraday Soc., **32**, 8 (1937).
[6] Lennard-Jones, Proc. Roy. Soc., **A107**, 636 (1935).
[7] M. Goeppert-Mayer and G. Kane, J. Chem. Phys. **8**, 642 (1940).
[8] These calculations were made by the Computation Laboratory of the National Bureau of Standards, New York City, under sponsorship of the ONR.

The Sodium (^2P) Photo-Sensitized Decomposition of Ethane*

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October 19, 1949

THE excitation energy of the sodium (^2P) states is approximately 48.3 kcal.; the heat of formation of gaseous sodium hydride from the atoms is in the range 47[1] to 51.6[2] kcal. It might be expected, therefore, that, provided sodium hydride were formed, Na(^2P) atoms could sensitize the decomposition of hydrocarbons having C—H bond strengths not exceeding 95.3 to 99.9 kcal. The analogous reaction is known to occur with Cd($^3P_1$) atoms,[3] for which the excitation energy is 82.9 kcal. and the heat of formation of the hydride is 15.6 kcal.; in this case cadmium hydride bands were detected by resonance fluorescence.[4] Jungers and Taylor[5] made an unsuccessful attempt to sensitize the polymerization of ethylene with Na(^2P) atoms, but it seemed reasonable to assume that their negative result was, by analogy with the data on