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Note on the Rigid Multi-Layer Postulate of Eversole and Lahr

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June 6, 1946

EVERSOLE and Lahr¹ have interpreted certain electrokinetic measurements as indicating properties of rigidity in part of the double layer at solid-electrolyte interfaces, a view held by von Buzagh² and others. They have used¹ published zeta-potential figures to deduce and thicknesses of from 3A to 63A for the rigid layer in aqueous salt solutions, values which could be accommodated by classical double layer theory, although Bikerman³ is of the opinion that any rigid layer is caused by the inherent roughness of all solid surfaces. In a later experimental paper,⁴ Eversole and Lahr produce evidence which, it is claimed, substantiates the previous calculations and indicates a rigid layer of thickness about 100A for water against quartz.

In the experiments of Eversole and Lahr the "distance of separation," 'air, between a quartz lens and plate placed together in air was determined interferometrically. Water was then condensed between the lens and plate and the new "distance of separation," 'water, determined. Negative values both for 'air and 'water were obtained, but it was assumed that the subtraction of 'air from 'water eliminated the error to which the negative values were due, and gave the thickness of the rigid layer. The validity of this assumption is to be questioned, in view of the very large variations in the individual values of 'air and 'water. The results obtained by Eversole and Lahr (five in number) are given in Table I.

Although the deviation from the mean in each series is as much as 600A, the conclusion drawn is that the total layer thickness, "subject of course to considerable experimental error," is about 200A. Since this involves two interfaces, the layer thickness at one surface is taken as 100A.

If now Students "t-test" for significance of differences between means of small populations, as described by Evans⁵ is applied to the above results, there is indicated approximately a 75 percent probability that the difference between the means of the two series in Table I is not significant, because of the wide variation within each series.

Using an interferometric principle similar to that of Eversole and Lahr and a more developed technique, details of which will be published later, the writer has found no evidence for the presence of these layers in water, methyl alcohol or toluene. Some of the results obtained are given

TABLE I.

Expt.	'air A	'water A	"Layer thickness" ('water - 'air) A
1	-1210	-870	330
2	-950	-800	160
3	-90	+140	230
4	-1160	-840	320
5	-350	-220	130
Mean	-752	-518	234

in Table II. (In the last column of this table, *P* indicates the approximate probability of insignificance in the difference of the means, as determined by Students "t-test".)

TABLE II.

Liquid	Expt.	'air A	liquid A	(liquid - 'air) A	<i>P</i>
Water	1	20	15	-5	98%
	2	-5	5	10	
	3	-5	0	5	
	4	10	0	-10	
	5	0	5	5	
	Mean	4	5	1	
Methyl alcohol	1	5	-5	-10	75%
	2	25	-5	-30	
	3	10	10	0	
	4	-10	0	10	
	5	-10	-5	-5	
	Mean	4	-1	-5	
Toluene	1	-10	-10	0	95%
	2	0	-5	-5	
	3	0	20	20	
	4	15	20	5	
	5	15	5	-10	
	Mean	4	6	2	

A further investigation of the subject is in progress, using air bubbles against quartz after the manner of Derjaguin,⁶ who reports the presence of thick interfacial films on glass and mica in water. In view of the recent work of Tolansky,⁷ any interferometric work on "smooth" mica cleavage planes must be viewed with suspicion, since variations in surface level of the order of several thousand angstroms may exist.

¹ W. G. Eversole and P. H. Lahr, *J. Chem. Phys.* **9**, 530 (1941).² E.g., A. von Buzagh, *Colloid Systems* (Technical Press Ltd., London, 1937), pp. 153-4.³ J. J. Bikerman, *J. Chem. Phys.* **9**, 880 (1941).⁴ W. G. Eversole and P. H. Lahr, *J. Chem. Phys.* **9**, 686 (1941).⁵ U. R. Evans, *Chem. Ind.* **14**, 106 (1945); see also L. H. C. Tippell, *Methods of Statistics* (Williams and Norgatt Ltd., London, 1941), pp. 112-3.⁶ B. Derjaguin and M. Kussakov, *Acta Physicochimica* **10**, 25 (1939); B. Derjaguin and M. Kussakov, *Acta Physicochimica* **10**, 153 (1939).⁷ E.g., S. Tolansky, *Proc. Roy. Soc. A* **184**, 41 (1945); S. Tolansky, *Proc. Roy. Soc. A* **184**, 51 (1945).

Bond Hybridization in the Non-Tetrahedral Carbon Atom

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June 17, 1946

INASMUCH as Duffey's calculations³ lead to the prediction of 180° H-C-H angles in cyclobutane and cyclopropane (and possibly ethylene) which we do not think reasonable, we are presenting a somewhat similar calculation which we had made and which gives more reasonable results.

Duffey calculates *s*, *p* hybrids with maxima in the directions of the required bonds. However, considerably stronger bonds can be formed by dropping this requirement and assuming that bond strength is proportional to the value of the orbital in the desired direction, whether or not the maximum of the orbital lies in this direction.

The orbitals *f*₁ and *f*₂ were used to form the two carbon-carbon bonds whose angle is determined by the geometry of the molecule. The directions of the other two bonds are

taken in directions of the maxima of f_3 and f_4 . With no loss in generality and a considerable gain in the simplicity of the equations, orbitals f_1 and f_2 can be chosen with their maxima in the xz plane, equally inclined to the z axis. By symmetry, f_3 and f_4 then lie in the yz plane, also equally inclined to the z axis.

Applying the usual normalization and orthogonality conditions we have:

$$f_1 = as + bp_z + (1/2)^{1/2} p_x, \quad (1)$$

$$f_2 = as + bp_z - (1/2)^{1/2} p_x, \quad (2)$$

$$f_3 = bs - ap_z + (1/2)^{1/2} p_y, \quad (3)$$

$$f_4 = bs - ap_z - (1/2)^{1/2} p_y, \quad (4)$$

$$b = +(\frac{1}{2} - a^2)^{1/2}. \quad (5)$$

We now determine the value of a (and b by Eq. (5)) so that f_1 will have the maximum value in a particular direction θ_0 in the xz plane by setting $df_1/da = 0$. This requires that

$$a = \left(\frac{1}{2 + 6 \cos^2 \theta_0} \right)^{1/2}, \quad (6)$$

$$b = \left(\frac{3 \cos^2 \theta}{2 + 6 \cos^2 \theta_0} \right)^{1/2}. \quad (7)$$

The angle θ_{34} between the bonds formed with the orbitals f_3 and f_4 is given by the expression:

$$\tan \theta_{34} = \frac{-2(1 + 3 \cos^2 \theta_0)^{1/2}}{3 \cos^2 \theta_0}. \quad (8)$$

We have calculated the H-C-H angle, θ_{34} , and bond strengths, f_{01} and f_{03} , for several values of $2\theta_0$, the C-C-C angle (Table I). Assuming bond energies proportional to

TABLE I.

$2\theta_0$ ($=\theta_{12}$)	Strength of bonds (1) and (2) f_{01}	θ_{34}	Strength of bonds (3) and (4) f_{03}
0°	1.414	126° 52'	1.982
60°	1.887	121° 58'	1.989
90°	1.984	115° 23'	1.995
108°	2.000	109° 58'	2.000
109° 28'	2.000	109° 28'	2.000
120°	1.996	105° 50'	1.998
180°	1.932	90°	1.732

square of bond strength and using¹ 59 and 87 kcal. for normal C-C and C-H bond energies, we obtain 10 and 2 kcal. as the strain energies per CH₂ group of cyclopropane and cyclobutane in fair agreement with experimental values of about 10 and 4⁵ (estimated from cyclobutane derivatives). Probably about 2 kcal. should be added to the calculated values for torsional strain.⁶ The energy calculation does not apply to ethylene because the bond is much shorter than it is in normal paraffins.

That the exterior angle in cyclopropane is not 180° as suggested by Duffey is shown conclusively by the large dipole moment of 1,1-dichlorocyclopropane.⁷ Also, the calculation Duffey quotes from Herzberg⁸ is incorrect. The correct C-C distance for 180° angle is 1.616 Å not 1.556 Å. The moment of inertia of cyclopropane is fitted, for example, by $r_{C-C} = 1.530$ Å (electron diffraction),

$r_{C-H} = 1.070$, $\angle H-C-H = 125^\circ$. No unique angle is obtained from one moment of inertia. Finally, Donohue *et al.*⁹ find $120^\circ \pm 8^\circ$ for $\angle HCH$ in spiropentane. The electron diffraction of 1,1-dichlorocyclopropane would determine this angle.

In conclusion, it should be pointed out that the ideas of s, p hybridization and proportionality of energy to f^2 are approximations, and the agreement of these calculations with experiment is to a great extent fortuitous. For this reason, we did not attempt any further refinements such as simultaneous maximization of C-C and C-H bond energies.

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² National Research Fellow in chemistry.

³ G. H. Duffey, J. Chem. Phys. **14**, 342 (1946).

⁴ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940).

⁵ G. E. K. Branch and M. Calvin, *Theory of Organic Chemistry* (Prentice-Hall, Inc., New York, 1941), p. 279.

⁶ K. S. Pitzer, Science **101**, 672 (1945).

⁷ M. T. Rogers and J. D. Roberts, J. Am. Chem. Soc. **68**, 843 (1946).

⁸ G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand, New York), p. 440. The C-C distance given for 120° is also incorrect.

⁹ J. Donohue, G. L. Humphrey, and U. Schomaker, J. Am. Chem. Soc. **67**, 332 (1945).

Electronic Shifts at Moderate Temperatures in Metals of Group VIII

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FURTHER evidence has been secured, supplementing that offered some years ago for pure iron,¹ of what are believed to be specific electronic shifts in iron within ordinary temperature ranges. Similar series have also been established for all the other Group VIII metals by measurements of either the electrical resistance of pure or alloyed metal wires or of the electrolytic conductivity of glasses containing these metals. For all the metals, the temperatures of the discontinuities follow, within experimental limits, the simple Ritz formula:

$$T_k = ct[(1/n_0^2) - (1/n^2)],$$

where ct is a constant which is different for each metal; n_0 has the value 3 for Fe, Co, Ni, 4 for Ru, Rh, Pd, and 5 for Os, Ir, Pt; and n , for each metal, has the successive values $n_0 + 1$, $n_0 + 2$, ... ∞ .

No change was found in the critical temperatures either with concentration or with the form of chemical combination. Hence the effect is believed to be a purely atomic phenomenon.

The fact that the Curie magnetic transition temperatures of Fe, Co, and Ni, all occur exactly at some definite term in the appropriate series indicates that the data may be of great importance in clarifying the theory of ferromagnetism.

Further details will be published shortly.

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¹ C. B. Post and W. R. Ham, J. Chem. Phys. **5**, 913-919 (1937).
W. R. Ham and W. L. Rast, Trans. A.S.M. **26**, 885-902 (1938).