At present there seems to be no adequate theoretical method for calculating the free energy of ionization of an organic acid,[11] hence methods which have been suggested for calculating or representing the effect of substituents upon the ionization constant of such an acid are approximate. While Smallwood[12] met with some success by attributing the change to the electric moment associated with the substituent, he obtained particularly bad results with the acids studied in this paper. MacInnes[13] has shown that log K for certain substituted acids, including the ones here studied, is nearly a linear function of d^{-1}, where d is taken as the distance between the polar bond joining the carboxyl group to the chain or ring and the polar bond connecting the substituent to the chain or ring. If the d's be taken as the ratios of the distances across a regular plane hexagon for the *ortho*, *meta* and *para* acids, namely, $1:\sqrt{3}:2$, these three acids give a straight line when log K is plotted against d^{-1} and the equation for the line is

$$\log K = -5.0471 + (2.1249/d) \qquad (16)$$

This equation reproduces the values of K to within ±0.31%, but, as MacInnes has observed, the constant is not log K for the unsubstituted acid. This behavior of the substituted acids might be considered to point to a plane, regular, hexagonal structure for these substances, but, even if the relation used could be developed in a forthright way, the values of log K for the *meta* and *para* acids are so nearly equal that this indication should be given little weight. Our own attempts to develop an exact theory of the ionization of the weak electrolyte have been unsuccessful.

Summary

The conductances of aqueous solutions of benzoic acid, *o*-chlorobenzoic acid, *m*-chlorobenzoic acid, *p*-chlorobenzoic acid and the sodium salts of the first three acids have been measured at 25°.

From these results and our previous measurements on hydrochloric acid and its sodium salt the following ionization constants have been found

$C_6H_5COOH \quad K = 6.295 \times 10^{-5}$
$o\text{-}ClC_6H_4COOH \quad K = 1.197 \times 10^{-3}$
$m\text{-}ClC_6H_4COOH \quad K = 1.506 \times 10^{-4}$
$p\text{-}ClC_6H_4COOH \quad K = 1.04 \times 10^{-4}$

The results with the strong electrolytes again confirm Onsager's equation as a limiting law and Shedlovsky's extension of the equation to the moderately dilute solutions. The results with the weak acids again show that the theoretical constant of the limiting law of Debye and Hückel correctly represents the dependence of the activity coefficient of these acids upon their ionic concentrations.

At present, there is no adequate theoretical method of calculating the ionization of a weak electrolyte from its structure.

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(11) For a discussion of the several factors involved see Briegleb, *Z. physik. Chem.*, **10B**, 205 (1930).

(12) Smallwood, THIS JOURNAL, **54**, 3048 (1932).

(13) MacInnes, *ibid.*, **50**, 2587 (1928).

NOTES

Notes on the Movement of a Borax Bead on Platinum Wire

BY J. L. CULBERTSON

Anyone who has had occasion to use the borax bead on a platinum wire in the qualitative laboratory is familiar with the method by which the bead may be driven from one part of the wire to another by means of the flame. This is accomplished by heating one side of the bead on holding it in the edge of the flame. So heated the bead will recede from the hotter side and by drawing the wire through the flame as rapidly as the bead recedes the movement may be continued to the end of the wire. This phenomenon is exceedingly common and yet the writer has been unable to find in the literature any analysis of the situation based on a consideration of the surface tensions acting in the system. That such an analysis may be appropriate is suggested by the observation that the contact angle of the liquid bead on the surface of the platinum is much greater when at high temperatures than when at lower ones. No measurements of these contact angles have been made but the fact that the angle changes, as indicated, with temperature change is readily verified by even the most casual observation. This may be most readily accomplished by studying the form of a small globule of borax on a piece of platinum foil. When enveloped in a Bunsen flame the globule will draw up into a form almost hemispherical but on withdrawing it from the region of high temperature the borax is observed to spread into a comparatively thin layer. The spreading is probably arrested by the increased viscosity and rigidity of the cooling mass. The bead on the wire may, somewhat less readily, be observed to undergo the same changes.

Let us consider an application of the equation of Thomas Young to the point of contact of the bead with the platinum wire. This equation reads as follows: $S_1 = S_{12} + S_2 \cos \Theta$, where S_1 is the surface tension of the solid, S_{12} is the interfacial surface tension (solid–liquid), S_2 is the surface tension of the liquid and Θ is the angle of contact of the liquid with the solid. Of course the equation cannot be applied quantitatively but the significance of a change in Θ can be estimated. Rewriting the equation as $S_1 - S_{12} = S_2 \cos \Theta$ it seems apparent that an increasing value of Θ indicates that the $S_1 - S_{12}$ difference is decreasing more rapidly that the surface tension of the liquid, or in other words the adhesion tension[1] of the borax–platinum system is decreasing with increase of temperature.

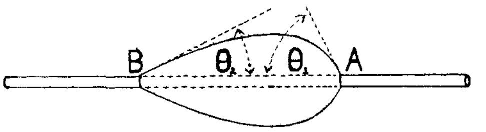

Fig. 1.

Now referring to the figure and assuming that heat is applied at A it is obvious that an increase in the contact angle Θ_1 on the hot side of the bead will tend to shorten the longitudinal dimension of the latter, causing it to swell and thereby increase the angle Θ_2 on the cool side of the bead. Furthermore, it is to be expected that the surface tension of the liquid will be lower on the hot side of the bead than on the cool side and on this account the surface layer of the drop will be drawn toward B. This will also tend to increase the angle Θ_2 except in so far as the surface movement is offset by the counter-circulation within the bead. The increase in Θ_2 at B will alter conditions at that point and if a dynamic equilibrium actually existed there, readjustment will be made by the movement of the line of contact toward the left, which will tend again to lower the magnitude of the angle Θ_2. If therefore a temperature differential is maintained between A and B, this readjustment process will be made continuous and the bead will creep along the wire from hot to cool regions. This latter is exactly what we find does occur and our analysis seems to indicate that in such a system the formation of contact angles is the result of a dynamic equilibrium of surface forces.

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[1] Freundlich, "Colloid and Capillary Chemistry," p. 157.

The Preparation of Phenyl Mercuric Nitrate

BY G. H. WOOLLETT AND V. A. COULTER

Diphenyl mercury in chloroform when shaken vigorously with aqueous mercuric nitrate solution is converted into phenyl mercuric nitrate. The entire mixture may later be dissolved in boiling alcohol for crystallization, giving a 75% yield of nearly pure material, m. p. 188° dec. The residue left after melting decomposes explosively at about 270°. The following quantities have proved to be in best proportion: $HgNO_3 \cdot 0.5H_2O$ 3.49 g., chloroform 50 cc., diphenyl mercury 3.54 g. (0.01 mole), water 3 cc. and alcohol 600 cc. The solubility of phenyl mercuric nitrate at 5° and at the boiling point of the solvent (g. per 100 cc.) is as follows: water 0.05; 0.90; alcohol 0.08; 0.51.

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An Unknown Radioactivity

BY A. V. GROSSE

Three years ago, during our unsuccessful search of an isotope of element 91 of long life,[1] we noticed in two zirconium minerals (eucolite and eudyalite from Greenland) a small α-activity, which behaved chemically identically or very like protactinium, the origin of which was difficult to account for.

In the meantime the relationship between protactinium and uranium has been definitely established and the fact confirmed that in every uranium mineral, disregarding age, origin or uranium concentration, 1 g. of uranium contains in equilibrium $2.7_8 \cdot 10^{-7}$ g. of Pa, equalling $27._9$ mg. of U_3O_8 in α-activity.[2,3]

In the minerals mentioned the amount of α-

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[1] A. V. Grosse, *Naturwissenschaften*, **20**, 505 (1932).

[2] A. V. Grosse, *Phys. Rev.*, **42**, 565 (1932).

[3] A. V. Grosse, *J. Phys. Chem.*, **38**, 487 (1934).