in the line, so that the distance between two adjacent peaks corresponds to the time occupied by half an alternation. The wave may be slightly altered in form and amplitude by trying different signals and by altering the wattage of the lamp in circuit, but care must be taken not to burn out the coil.

In Medford, Mass., the local current is 110 v. 60 cycle A.C.; thus the distance between two peaks corresponds to a time interval of 1/120 second. The rate of alternation in A.C. current is very constant, and the above arrangement has been found very satisfactory, particularly for student use. It is accurate and simple and requires no attention or delicate adjustment.

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SPECIAL ARTICLES

CONTRASTING PROPERTIES OF IONS, ZWITTERIONS AND UNCHARGED MOLECULES[1]

Apparent molal volume: The great density of such constituents of biological systems as amino-acids and most proteins depends largely upon the electrical charges borne by these molecules. Molecules can not be said to exist in the inorganic crystal, where each ion is related to all others surrounding it. By contrast the distances separating atoms within molecules of an uncharged organic crystal are far smaller than those between atoms of adjacent molecules.[2] Intermediate in behavior are the zwitterions recognized by Bjerrum[3] just a decade ago as being neither electrolytes nor uncharged molecules. Of great importance in physiology and morphology these charged molecules are closely packed and the density of the smallest of them, glycine, is 1.61 in the solid state.

The densities not only of amino-acids, but of certain proteins[4] appear to be greater in dilute solution than in the solid state. This results from electrostriction of the solvent, estimated to be approximately ten cc per mole per charge when these are widely separated from each other.[5] Electrostrictions of this magnitude are produced by ions slightly greater in radius than 2 Å. The smallest of the zwitterions, glycine, has a radius of 2.8 Å. When the positive $-NH_3^+$ group is separated from the COO^- group by only one carbon atom, as in all neutral α amino-acids, the combined electrostrictive effect is reduced to 13.4 cc per mole.[6]

Influence of concentration upon apparent molal volume: Not only the closeness of approach of charged groups in the same molecule, but increase in concentration of the solution increase the apparent molal volume. This increase has been shown to be proportional to the square root of the concentration for salts, and also for cane sugar and urea,[7,8] though these molecules do not bear electrical charges, as may be demonstrated from the density of their solutions.[6] That the square root law holds for the latter substances[9] because of the polarity of the hydroxyl and amino groups is strongly suggested by study of aliphatic acids containing various substituents. Acetic acid does not obey the square root law, and increasing the length of the hydrocarbon chain, as in propionic, butyric and valeric acids, increases the deviation from linearity. Chloracetic acid, in which the strongly electronegative chlorine atom is substituted for a hydrogen atom, does, however, obey this law, as do di- and trichloracetic acids $(\frac{\delta\Phi}{\delta\sqrt{c}}=1.55$, 3.12, 6.00). Substituents which increase electrolytic dissociation appear also to increase the proportionality constant $(\frac{\delta\Phi}{\delta\sqrt{c}})$ relating the apparent molal volume to the square root of the concentration.

Glycine, which contains the electronegative amino group, obeys the square root law and so do its hydrochloride and sodium salts $(\frac{\delta\Phi}{\delta\sqrt{c}}=1.52$, 2.54, 3.89). Neither amino-acids of long hydrocarbon chains nor their hydrochlorides or sodium salts obey this law, however, but behave in this respect rather like aliphatic acids. The salts of amino-acids as of aliphatic acids must, however, be considered largely dissociated in solution. Thus the square root law appears to depend largely upon the polarity of the groups in the molecule.

The apparent molal volume of β alanine increases approximately with the first power of the concentration rather than with its square root. This is also true of glycyl-glycine, which contains the polar amide linkage, and of the sodium salt of ε amino caproic

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[1] Abstract of paper read at the meeting of the National Academy of Sciences in Cambridge, November 22, 1933.

[2] S. B. Hendricks, *Chem. Rev.*, 7: 431, 1930.

[3] N. Bjerrum, *Z. Physik. Chem.*, 104: 147, 1923.

[4] H. Chick and C. J. Martin, *Biochem. Jour.*, 7: 92, 1913.

[5] H. H. Weber, *Biochem. Z.*, 218: 1, 1930.

[6] E. J. Cohn, T. L. McMeekin, J. T. Edsall and M. H. Blanchard, *Jour. Biol. Chem.*, 100, Proc. xxviii, 1933.

[7] W. Geffcken, *Z. Physik. Chem.*, 155: 1, 1931.

[8] F. T. Gucker, *Chem. Rev.*, 13: 111, 1933.

[9] The melting points of cane sugar (186° C.) and of urea (133° C.) are also higher than those of most uncharged molecules. The amino-acids melt in the neighborhood of 300° C. and neutral salts at still higher temperatures.

acid. The sodium salt of glycyl-glycine behaves in a manner intermediate between the sodium salt of glycine and of ε amino caproic acid. Despite its large dipole moment, the apparent molal volume of isoelectric ε amino caproic acid, with its long hydrocarbon chain, changes very little indeed in solutions containing less than 25 per cent. of amino-acid. This type of behavior is also characteristic of most proteins, whose great apparent density in solution diminishes but little even in the concentrations which obtain in biological systems.

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"EXERGIC" AND "ENDERGIC" REACTIONS[1]

IN the consideration of chemical reactions it is often necessary to distinguish between (a) those processes which occur spontaneously, for example, in a primary cell, that is, which are capable of doing work; and (b) those which require work to be done in order to bring them about, for example, the electrolytic decomposition of water into hydrogen and oxygen. Thermodynamically, these types of reaction are distinguished as resulting in (a) a decrease in free energy and (b) an increase in free energy.

It is proposed to designate these two types of reaction respectively as (a) "exergic," that is, capable of giving out work; and (b) "endergic," that is, taking in work. They are derived from the Greek root "ergon," work.

At first it might appear that the need for such terms is met by the customary expressions "exothermic" and "endothermic." It has long been known, however, that these terms are inadequate to describe chemical reactions, and hence the concept of free energies was introduced. As above noted, the new terms apply to the free energy and not to the total energy of the process. The majority of reactions that are exothermic are also exergic, and most of those that are endothermic are endergic, but the relation is not universal.

Thus, Lewis and Randall[2] cite a cell in which the reaction

$$\mathrm{Ag(s) + HgCl(s) = AgCl(s) + Hg(1)}$$

yields at 298° K a potential of 0.0455 V (that is, according to the above definition the process is exergic), although the chemical reaction is endothermic, with a total heat change, $\triangle H_{298}$, equal to $+1280$ cal. In order for the cell reaction to occur spontaneously, heat must be taken from the surroundings.

Similarly, it follows that the reverse reaction

$$\mathrm{Hg(1) + AgCl(s) = Ag(s) + HgCl(s)}$$

is exothermic, that is, $\triangle H_{298} = -1280$ cal.; but in order for this process to occur in a cell, work equivalent to 0.0455 V must be done upon it, that is, the process is endergic.

The need for such terms was evidently felt by H. J. Creighton,[3] who states that chemical changes "are called 'exo-electrical' when they develop electrical energy and 'endo-electrical' when they absorb electrical energy." His terms have much the same meaning as those now proposed, but are somewhat less general in their application.

No new concepts are involved in the proposed terms. Justification for their use must be found in their conciseness or pedagogic convenience. The proposed definitions are as follows:

"Exergic reactions are those which occur with a decrease in free energy."

"Endergic reactions are those which occur with an increase in free energy."

W. BLUM

U. S. BUREAU OF STANDARDS

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[1] Publication approved by the director of the U. S. Bureau of Standards.

[2] "Thermodynamics," p. 174. McGraw Hill Book Co., New York, 1923.

[3] "Principles and Applications of Electrochemistry," Vol. 1, 2nd ed., p. 8. John Wiley and Sons, New York, 1928.

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