

expresses the distances from the last inert gas (partial lengths of the periods) and atomic numbers, respectively, of the subshell closing elements, so that, in the particular case of  $n = 1$ , the length of the complete periods and the atomic numbers of the inert gases are found.

The two equations correspond to previously obtained combinational expressions<sup>1</sup> which here have been given a most convenient simplification. By placing the periodicity term  $f(n + l)$  in algebraic form,  $L$  can reduce to the Tomkeieff's rule<sup>2</sup> ( $E = 0$ ;  $l = 1$ ), and  $Z$  becomes analogous to Hakala's law<sup>3</sup>. Thus they are shown to achieve wider generalization than the hitherto known formulæ.

Moreover, the close relationship established between  $L$  and  $Z$  constitutes synthetic mathematical evidence of a bidimensional double periodicity in the chemical table.

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<sup>1</sup> Marson, L. M., and Zucchi, U., *Atti Ist. Ven. Sci. Let. Arti*, **133**, 215 (1955); *Chimica* (in the press).

<sup>2</sup> Tomkeieff, M. V., *Nature*, **167**, 954 (1951).

<sup>3</sup> Hakala, R., *J. Phys. Chem.*, **56**, 178 (1952).

### Thermodynamic Interpretation of the Eötvös Constant

Eötvös<sup>1</sup>, in 1886, proposed the following equation for liquids

$$\gamma(Mv_{sp})^{2/3} = K_E(T_c - T) \quad (1)$$

where  $\gamma$  is surface tension,  $M$  is molecular weight,  $v_{sp}$  is specific volume and  $T_c$  is critical temperature, which is found to be strikingly valid over a wide range of temperature for most non-polar compounds. Even for polar compounds the equation is valid though to a more limited extent; but the value of the constant,  $K_E$ , is often very different from the usual value, 2.12. This empirical equation has been given some theoretical support (cf. Partington<sup>2</sup>). The purpose of the present communication is to point out a simple thermodynamic interpretation of the above equation.

Since the left-hand side of the equation is a free-energy term and the right-hand side is linear in  $T$ , its formal similarity with the standard thermodynamic equation,  $\Delta F = \Delta H - T\Delta S$ , is apparent. Based on this we can identify the Eötvös constant as the entropy of formation in proper units of  $(Mv_{sp})^{2/3}$  surface area starting from liquids in the interior. Since a mole of a liquid considered as a cube presents an area of any face equal to  $(Mv_{sp})^{2/3}$ , and since this cube can be divided into  $N^{1/3}$  such faces, the molar entropy is easily obtained by multiplying both sides of equation (1) by  $N^{1/3}$ . Converted into calories, we obtain the molar entropy of surface formation for non-polar compounds,

$$2.018 \times K_E \text{ cal./deg.} = 4.28 \text{ entropy units}$$

Thus we arrive at the interesting conclusion that the Eötvös constant is a measure of the entropy of formation of surface and the entropy change in bringing liquid molecules from the interior to the surface is the same for all non-polar liquids and nearly the same for all liquids, and is equal to 4.28 calories per degree per mole. In other words, the

Eötvös equation is the liquid-surface analogue of Trouton's law relating to vaporization.

It seems plausible that this excess entropy on the surface is almost wholly configurational, arising out of increased symmetry in the interior of a liquid and the non-spherical shape of liquid molecules. This idea is supported by the fact that the corresponding entropy changes for alcohols are much lower, being 1.88 for methyl alcohol and 2.18 for ethyl alcohol. This loss of entropy for polar liquids is thus to be ascribed to the well-known orientation of such molecules on the interface. This also agrees with the observation that mercury ( $K_E \simeq 1$ ), which presumably has more or less spherical molecules, has a lower Eötvös constant, and geometrically complicated molecules, for example, tripalmitin ( $K_E = 5.4$ ), have higher Eötvös constants.

Conversely, a thermodynamic deduction of Eötvös equation from the above assumption, the temperature independence of  $\Delta H$ , and the boundary condition of zero free-surface energy at the critical temperature, is simple and need not be elaborated here. The next step would be to investigate the possibility of deduction of the numerical value of  $K_E$  from statistical thermodynamics.

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<sup>1</sup> Eötvös, *Ann. der Physik.*, **27**, 448 (1886).

<sup>2</sup> Partington, J. R., "An Advanced Treatise on Physical Chemistry", **2**, 157 (Longmans, 1951).

### Oxidation-Reduction Potential of Modified Cytochrome *c*

THE presence of modified cytochrome *c* in the widely used Keilin and Hartree preparation was first reported by Margoliash<sup>1</sup>. Separation was effected by chromatography at pH 7.0 on a column of the resin 'Amberlite IRC-50'. Modified material was present to the extent of 10–25 per cent and was characterized by having a lowered enzymatic activity in the cytochrome oxidase (heart muscle) and succinic oxidase (kidney) systems but an increased rate of ascorbic acid oxidation. Visual spectroscopy, however, did not show any difference between this and other cytochrome *c* fractions. Evidence was presented that the modification was caused by the action of trichloroacetic acid on cytochrome *c* during the extraction procedure.

We have recently compared<sup>2</sup> the  $E'_0$  values at pH 6.4 and 25° C. of the usual Keilin and Hartree type preparation with cytochrome *c*, purified on a resin column, from both ox- and horse-heart muscle. It was suggested that the slightly higher value of the less pure samples (0.270 V.) compared with the resin-purified samples (0.255 V.) was due to the presence of modified cytochrome *c*. We have now determined the  $E'_0$  value of this material as separated by the above procedure from ox-heart cytochrome *c* and find it to be 0.310 V. under the same conditions of pH and temperature.

In order to attempt its complete modification, a sample of ox-heart cytochrome *c* purified on a resin column was subjected to prolonged treatment with trichloroacetic acid (2.5 per cent, 18 hr. at 25° C.), followed by dialysis against 0.5 per cent sodium chloride. The potential of the resulting pigment