

Letters to the Editor.

The Electric Discharge in Gases and the Debye-Hückel Theory.

IN view of the remarkable success of the Debye-Hückel theory in the field of the kinematics of ions in liquid media, it is not a little surprising that but little use of its methods has been made in the analysis of the phenomena in the discharge tubes. The object of the present note is to direct attention to a possible treatment of the familiar cathode-fall effects from the standpoint of the theory.

It is easily shown that even in the intense¹ type of electric discharge the condition of the gas at these low pressures is analogous to that of an electrolytic solution at great dilutions. For simplicity, the case of singly charged positive and negative ions will be considered here. Making the same assumptions as made by Debye-Hückel² in the development of their theory, we arrive at a similar differential equation:

$$\text{div grad. } V = \nabla^2 V = K^2 V \quad \dots (1)$$

for which a solution is now sought, having cylindrical symmetry. In the above equation K is a constant and V is the potential at any point (r, z, ϕ) , V being supposed to be such that power terms of $\frac{eV}{kT}$ higher than the first can be neglected (where e , k and T have their usual significance) *i.e.*, $V \gg 30$ kv for ordinary temperatures.

The solution obtained is

$$V = [A + A'e^{Kz}] [B - \frac{B'r^2}{c^2} - \dots] \quad (2)$$

where c is the radius of the discharge tube and A , A' , B and B' are constants, to be evaluated from initial conditions. The conditions of the problem are assumed to be such that when $z = 0$, $V = 0$, $(\frac{\partial V}{\partial z})_{z=0} = 0$.

Applying this equation to the variation of the length of the cathode-fall with the voltage-drop across it, it will be easily seen that the former will vary as the logarithm of the latter. This is actually found to be the case as a first approximation, in the experiments on cathode-fall length for varying voltages using positive rays of hydrogen.³

The theory can easily be extended to take into account the different types of ions present, the effect of the space charge at the cathode, the perturbation of the equilibrium conditions due to the passage of the current, etc., to be treated elsewhere.

In the end, it should be remarked that the chief value of the Debye-Hückel procedure lies in the fact, that it does not contemplate any specific kinematical picture of the reactions going on in the system, but makes use of only general statistical methods.

Physical Laboratory, V. T. CHIPLOKAR,
Benares Hindu University,
December 19, 1935.

¹ Townsend, J. S., "Electricity in Gases," Oxford, 1915; Millikan, Gottschalk and Kelly, *Phys. Rev.*, 1920, 15, 157.

² Taylor, H. S., "Treatise on Physical Chemistry," Macmillan & Co., Second Edition, I, 785.

³ Dasannacharya, B., and Das, G. K., *Proc. Ind. Sci. Cong.*, 1936, Indore, Phys. and Math. Section.

A Zonal Effect in the Electrolytic Coagulation of Colloid Manganese Dioxide.

EARLIER results¹ for the viscosity changes consequent upon the *slow* coagulation of a number of sols have shown the difficulty of reconciling experimental results with the chief assumption made in Smoluchowski's theory² of the kinetics of coagulation, *viz.*, that the change is but a time continuous coalescence of the micella. An additional support to this criticism was afforded in the measurement of μ the refractive index of a number of sols during coagulations. The curves in Fig. 1 show the course of μ -change

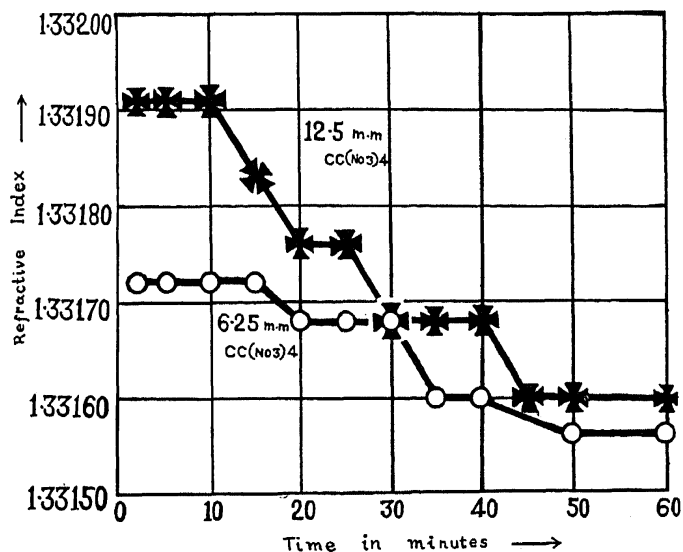


Fig. 1.

during two typical coagulations of the above sol by solutions of cerium nitrate. On general considerations it is seen that μ depends upon the total optical path for a given light beam passing through the colloid. This, in part, is constituted by the dispersed material. It is expected, therefore, that μ would alter due to micellar changes during

coagulation. The curves in Fig. 1 show in a striking manner the essential discontinuity characteristic of the course of the reaction, observed with a means markedly different from that employed previously.¹ This appears to be a general result at any rate in the *slow* region, as judged from data of over 80 cases examined in these Laboratories. Its prediction constitutes one of the chief criteria of the validity of any theory for both the kinetics and the mechanism of coagulation.

S. S. JOSHI.

Department of Chemistry, S. JAYA RAO.
Benares Hindu University,
Benares,
December 30, 1935.

¹ Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, **10**, 329; Joshi and Menon, *ibid.*, 1933, **10**, 599; Joshi and Nanjappa, *ibid.*, 1934, **11**, 133; Joshi and Iyengar, *ibid.*, 1934, **11**, 555, 573; Joshi and Panikkar, *ibid.*, 1934, **11**, 797; also *Journ. de. Chim. Phys.*, 1935, **32**, 455.

² *Z. Phys. Chem.*, 1917, **92**, 129.

The New Orienting Rule of Svirebely and Warner.

THE new empirical rule in aromatic substitution, recently enunciated by Svirebely and Warner¹ as generally applicable, connecting the electric moment of the benzene derivative and the directive power, is open to many objections.

Claiming that there were only three definite exceptions to the rule, *i.e.*, the cases of benzoic acid, methyl and ethyl benzoates for which moments less than 2.07 D have been recorded,² the authors, apparently to justify their rule, have revised the moments of the last two compounds to 2.43 and 2.52 respectively and have advocated a redetermination in the case of benzoic acid. Without digressing about the validity of the experimental method adopted in their revision, we point out that Bergmann and Weirmann³ could, once more, only obtain the value of 1.91 for methylbenzoate and from what follows, it can be inferred that the rule is not based on grounds too solid to predict with certainty a moment greater than 2.07 D either for benzoic acid or for these esters.

Leaving aside the notorious case of the nitrosogroup, it is pointed out that benzoin,⁴ deoxybenzoin,⁵ and dibenzylketone,⁶ which have been classified by the authors as *meta* directing in accordance with their rule because of their moments 3.4, 2.95 and 2.65 respectively, have actually been found to have the opposite effect! The failure of

the rule in these cases is strictly in accordance with the expectation of the modern theories of aromatic substitution,⁷ and is not to be attributed to any of the factors referred to by the authors. It can also be predicted safely that the rule is bound to fail in the cases of the substituents like $-\text{CH}_2.\text{CH}_2.\text{CO}.\text{C}_6\text{H}_5$, $-\text{CH}_2.\text{SO}.\text{C}_6\text{H}_5$, $-\text{CH}_2.\text{SO}_2.\text{C}_6\text{H}_5$, $-\text{CH}_2.\text{SO}_2.\text{CH}_2.\text{C}_6\text{H}_5$, etc., all of which are expected to possess moments higher than 2.07 D but direct only to *ortho* and *para*.

Further, the following substituents have all been found to be *ortho* and *para* directing; but possess moments⁸ greater than 2.07 D: $\text{CH}:\text{CH}.\text{CHO}$ ⁹ (3.71); $-\text{CH}_2.\text{CN}$ ¹⁰ (3.56); $-\text{CH}:\text{CH}.\text{CO}.\text{CH}_3$ ¹¹ (3.3); $-\text{N}(\text{NO}).\text{C}_6\text{H}_5$ ¹² (3.39); $-\text{SCN}$ ¹³ (3.00).

The dipole moment of the molecule can be claimed to bear a direct relation, as suggested in the rule, to the directive capacity of the substituent only if, according to the Robinson-Ingold theory of aromatic substitution, it decides the electronic disposition, as governed by the general polar and tautomeric effects, of the bond between the nuclear carbon and the attached atom of the substituent group. But this is not the case always¹⁴ particularly with complex substituent groups, where the rule has been shown to fail. If we consider the directive capacity of a *meta* directing group R with a high moment (*e.g.*, NO_2 , CN , $\text{SO}_2\text{R}'$) when attached to the ring through methylene groups (as in $-\text{CH}_2.\text{R}$, $-\text{CH}_2.\text{CH}_2.\text{R}$), we find that even by the intervention of one carbon atom between R and the ring, the substituent becomes *ortho* and *para* directive, though the moment remains but little altered. Thus it is clear that this "measurable property of the molecule," the dipole moment, can be connected with the directive power only with strict limitations.¹⁵

K. GANAPATHI.

Department of Organic Chemistry,
Indian Institute of Science,
Bangalore,
January 11, 1936.

¹ *J. Am. Chem. Soc.*, 1935, **57**, 655.

² Table of Dipolemoments, *Trans. Farad. Soc.*, 1934, **30**, Appendix.

³ *J. Am. Chem. Soc.*, 1935, **57**, 1755.

⁴ Chattaway and Coulson, *J. Chem. Soc.*, 1928, 1081.

⁵ Pictet, *Ber.*, 1886, **19**, 1064; List, B., *ibid.*, 1893, **26**, 2452; Golubew, *ibid.*, 1878, **11**, 1939.

⁶ Manchot and Krichsch, *Ann.*, 1904, **337**, 176; Manchot and Zahn, *ibid.*, 1906, **345**, 331.

⁷ Waters, *Chem. Rev.*, 1930, **7**, 409, 420.

⁸ Cf. ref. 2 for the moments recorded,