



Molecular theory of diffusion and electrolysis

E. Riecke

To cite this article: E. Riecke (1891) Molecular theory of diffusion and electrolysis, Philosophical Magazine Series 5, 32:199, 562-564, DOI: [10.1080/14786449108620224](https://doi.org/10.1080/14786449108620224)

To link to this article: <http://dx.doi.org/10.1080/14786449108620224>



Published online: 08 May 2009.



Submit your article to this journal [↗](#)



Article views: 2



View related articles [↗](#)

LXVII. *Intelligence and Miscellaneous Articles.*

MOLECULAR THEORY OF DIFFUSION AND ELECTROLYSIS.

BY E. RIECKE.

FOR a dilute solution of a body which is not an electrolyte, the concentration of which is constant in all plane layers which are at right angles to an axis (*z*-Axis), but is variable in the direction of this axis, the author finds that the excess of the molecules moving downwards (that is, the strength of the diffusion-current) is

$$S = \frac{lu}{3} \frac{\partial N}{\partial z};$$

in which *l* is the mean path of the dissolved molecules, *u* the molecular velocity, *N* the number of gramme-molecules in unit volume of the solvent; then *S* is the number of gramme-molecules which move through unit section in a second in the direction of decreasing concentration. The coefficient of diffusion *k* for the time of a day is therefore

$$k = 86400 \cdot lu/3.$$

Thus the author calculates:—

| | <i>k</i> . | Molecular weight. | <i>l</i> in cm. 10 ⁻⁸ . |
|---------------------|------------|-------------------|------------------------------------|
| Urea | 0.81 | 60 | 0.086 |
| Chloral hydrate ... | 0.55 | 165 | 0.094 |
| Mannite | 0.38 | 182 | 0.068 |
| Cane-sugar | 0.31 | 342 | 0.077 |

For electrolysis Prof. Riecke finds for the number *Q_p* of positive ions which pass in a second through unit section,

$$Q_p = \frac{N}{\tau_p} \frac{\epsilon l_p^2}{\mu_p u_p^2} Z;$$

in which *N* is the number of molecules in unit volume, *ε* the quantity of positive electricity united to each molecule, *l* the mean path, *u* the molecular velocity, *μ* the molecular weight, *τ* the time between two successive impacts of a molecule of the ion against a molecule of the solvent, and *Z* the E.M.F. in electrostatic measure. The suffix *p* signifies that the numbers refer to the positive ion; *n* in like

manner represents the negative ion. From this may be calculated the transfer-number and the conductivity. If, further, A is that quantity of hydrogen which is liberated in a second by a current of unit strength in electromagnetic measure, the molecular conductivity, L , expressed in electrochemical equivalents, is

$$L = \frac{1}{A} \left(\frac{l_p}{\mu_p u_p} + \frac{l_n}{\mu_n u_n} \right).$$

If U and V are the absolute mobilities of the ions, then $L = U + V$, and therefore

$$U = \frac{l_p}{A \mu_p u_p}, \quad V = \frac{l_n}{A \mu_n u_n}.$$

With the aid of the values of U and V given by Prof. Kohlrausch the author thus calculates:—

Positive Ions.

| | H. | Li. | NH ₄ . | Na. | K. | Ag. |
|---------------------|------|------|-------------------|------|------|-------|
| $U \ 10^{13}$ | 300 | 22.6 | 51 | 33.5 | 52 | 43 |
| μ_p | 1 | 7 | 18 | 23 | 39 | 107.7 |
| $l_p \ 10^9$ | 0.82 | 0.16 | 0.59 | 0.44 | 0.89 | 1.22 |

Negative Ions.

| | F. | CN. | Cl. | C ₂ H ₃ O ₂ . | NO ₃ . | Br. | ClO ₃ . | I. |
|---------------------|------|------|------|--|-------------------|------|--------------------|-------|
| $V \ 10^{13}$ | 32.4 | 54 | 53 | 24.8 | 49.6 | 57.2 | 43 | 57.2 |
| μ_n | 19 | 26 | 35.4 | 59 | 62 | 79.8 | 83.4 | 126.5 |
| $l_n \ 10$ | 0.12 | 0.75 | 0.86 | 0.52 | 1.07 | 1.39 | 1.07 | 1.76 |

For the coefficient of diffusion of an electrolyte, finally, that is the number of gramme-molecules which with unit difference of concentration pass through unit section, the author finds

$$k = 40.1(1 + 0.00367t)nU \times 10^{10},$$

in which n is the transfer-number, and U the absolute mobility of the ion in question. Thus for hydrochloric acid, $n = 0.19$ and $U = 300 \times 10^{-13}$, and therefore $k = 2.44$. Observation gives 2.30. This example also proves the agreement between Riecke's equation and that which Nernst first gave for the connexion between the

conductivity and diffusion of an electrolyte.—*Zeitschrift für physikalische Chemie*, vol. vi. p. 564; *Beiblätter der Physik*, vol. xv. p. 370.

METHOD OF DETERMINING THE SURFACE-TENSION OF MERCURY.

BY H. SENTIS.

A rectangular plate of iron of the volume abc and the weight p floats on mercury; the actual dimensions were about $120 \times 8 \times 2$ c. millim. The depth h to which it sinks is determined by means of a spherometer. On the one hand, we have from the principle of Archimedes,

$$p = abhD + 2(a+b)F \cos \alpha;$$

in which D is the density of mercury, F the surface-tension, and α the edge-angle, and the second term on the right is the weight of the mercury which would fill up the groove about the plate. The error which is due to the corners may be eliminated by means of another plate of volume cde , and weight p' , immersed to the same extent, which gives exactly the same error. On the other hand, the well-known equation

$$h = \sqrt{\frac{2F}{D}(1 - \cos \alpha)}$$

holds, and by eliminating the error and the edge-angle we get the formula

$$F = \frac{Dh^2}{4} + \frac{[p_1 - p_2 - (ab - cd)hD]^2}{[d + b - c - d]^2 h^2 D},$$

from which observations give $F = 39.23$ mg.—*Journal de Physique*, vol. ix. p. 384 (1890).

ALLOTROPIC SILVER.

Mr. M. Carey Lea requests us to correct a typographical error occurring in his paper, entitled "Notes on Allotropic Silver," which appeared in our October number. In this paper in several places appears "protochloride" where photochloride is the correct reading. Silver photochloride is the name proposed some years ago by Mr. Lea for the coloured compounds resulting from the union of normal silver chloride with small quantities of subchloride in no definite proportion, but after the manner of lakes as specially described by him.—The violet substance resulting from the exposure of silver chloride to light is a photochloride.