

THEORY OF METALS

By PROF. P. GOMBÁS

Physical Institute of the University for Technical and Economic Sciences, Budapest

sea water as a control. Two other similar plants were banded about half-way up the thallus, beneath a number of fertile segments.

All the plants were collected twenty-four hours after treatment. The experimental plants were all more or less tinged with a reddish-brown colour for two or three inches above the wound (presumably owing to post-mortem changes due to the poisonous effect of the copper), the rest of the thallus being a clear brownish-green.

Similar experiments were set up with *F. vesiculosus* var. *divaricata*. These each had only six series of dichotomies and about thirty apices of a clear olive-green colour, thus presumably in active growth. In this variety large bladders occur at all dichotomies (excepting those at the lowest levels) as well as in opposite pairs on the wings. In the experiments, the highest well-formed angle-bladders were slit open at the top, filled with the mixture or moist sand and the whole enclosed, while allowing freedom to the young branches on either side.

On collection twenty-four hours later, the branches beyond the bladders were noticeably discoloured excepting at the extreme tips and in small patches at the edges, the others on the same plants, as on the control, remaining olive-green. Below the wound, only an occasional small patch of discoloration was seen.

The plants were all wrapped separately and packed loosely in a tin. In this condition they remained alive for 2-3 days, but their colour was noticeably darkened, with less contrast between the normal and poisoned areas. They were afterwards dried under light pressure.

Cross and longitudinal sections of the dried material were cut (without wetting the razor), placed in a freshly made solution of 10 per cent potassium ferrocyanide for 20-30 min. and examined in dilute glycerine. With this procedure, a marked brick-red colour was seen in the primary medullary filaments of the stipe (or midrib) and also in those secondary filaments surrounding the medulla which had a relatively wide lumen and dense contents. The thick-walled, narrow, secondary filaments had everywhere apparently escaped the poison. The copper was followed upwards nearly to the apex of the thallus of *F. vesiculosus* (that is, 3-4 cm.) and appeared to have travelled for about 6-7 cm. upwards in the basal region of the stipe of *F. serratus*. In the downward direction, on the other hand, there was little sign of transport, and this only for about 2 cm. (*F. serratus*) or less than half a centimetre (*F. vesiculosus*).

Further study of the dried material was deferred until the experiments could be repeated under conditions more favourable for prompt examination, but these results, fragmentary as they are, definitely point to an upward translocation of copper ions (and presumably also of other mineral ions) along the broader medullary filaments. Downward translocation of phosphates and other substances was inferred by Wille¹ from analyses of old and new regions of the thallus of certain *Laminariae*, but experimental demonstration of the path of transport has not been previously given, so far as I am aware, for any of the brown algæ. The method should be capable of further development.

IN several previous papers¹ I have developed a statistical model of the metals which gives an account of the metallic bond of the alkali and the alkaline earth metals, and permits the computation of the fundamental constants of these metals without the aid of empirical or semi-empirical parameters. According to this model, the metal is composed of the lattice of the positive metal ions and of a uniformly distributed electron-gas consisting of the negative metal electrons (valency electrons). The lattice energy—from which all further conclusions can be derived in a simple way—is assumed to consist of the energy of the metal electron-gas and the interaction energy between the metal electron-gas and the metal ions. The energy of the metal electron-gas is composed of the electrostatic interaction energy, the exchange energy, the correlation energy and the zero-point kinetic energy of the metal electrons according to Fermi. The interaction energy of the metal electron-gas with the metal ions can be divided into three parts: first, the electrostatic interaction energy; secondly, the increase of the kinetic energy as a consequence of the penetration of the metal electron-gas into the electron clouds of the ions; and thirdly, the energy resulting from the exchange interaction between the metal electrons and the core electrons.

This model of the metals can be brought into a more appropriate form for further development and applications if we calculate the interaction energy of the metal electrons with ions—instead of on the basis of the commonly used electrostatic potential V of the ion—on the basis of a modified potential according to a formula I have derived²:

$$\Phi = V - \frac{1}{2}(3\pi^2)^{2/3} \epsilon \alpha_H v^{2/3},$$

where ϵ denotes the positive elementary charge, α_H the smallest Bohr radius of the hydrogen atom and v the electron density of the ions. Using this modified potential, we have to compute the absolutely lowest energy state of the metal electrons in the field of this potential without taking into account the exclusion principle for the metal electrons with regard to the electron states occupied by paired core electrons. This means that we have to neglect the above-mentioned second interaction energy term, the increase of the kinetic electron energy, which leads to an essential simplification. The energy resulting from the exchange interaction of the metal electrons with the core electrons can be computed in exactly the same way as in the case of free atoms³.

Hence we may express the lattice energy, taking all energy constituents into consideration, in the following way:

$$U = A_0 + \frac{A_1}{R} + \frac{A_2}{R^2} + \frac{A_3}{R^3} + \frac{A_4}{R^4},$$

where R denotes the radius of the elementary sphere containing one metal ion, and the coefficients, $A_i \dots$, are constants independent of R ; their value is determined only by the distribution of the potential and the distribution of the electrons within the ions and by the number of the metal electrons (valency electrons) per atom. All these quantities can be easily calculated. The constant term A_0 is

¹ Léeman, A. C., *Nature*, 138, 1099 (1936).

² Gustafsen and Darken, *Amer. J. Bot.*, 24, 615 (1937).

³ Both, M. P., *K. Akad. Amst.*, 38 (1935).

⁴ Wille, N., "Schwendener's Bot. Untersuch.", 321 (1899).

given by a series expansion of the correlation energy of the metal electron-gas in powers of $1/R$.

From the lattice energy as a function of R , the radius of the elementary sphere R_0 , the lattice energy U_0 , the sublimation energy S , and the compressibility κ in the state of stable equilibrium can be computed in the same manner as in the publications quoted. It is further possible to compute the work function w according to $w = -\partial U/\partial z$, where z represents the number of metal electrons per metal atom. (It is quite easy to give U for the coefficients A_i as a function of z .) Based upon the Thomas-Fermi-Dirac model of the metal ions, we get, without the help of empirical or semi-empirical parameters for the alkali metals, the data recorded in the accompanying table. R_0 is expressed in 10^{-8} cm., U_0 and S in k.cal./gram-atom, w in e-volts and κ in 10^{-12} cm.²/dyne units; and I should like to emphasize that U_0 , S , w and κ were computed by using the theoretical values of R_0 . This statistical model cannot be employed in the case of lithium, because in that metal the number of the core electrons is too small.

		Na	K	Rb	Cs
R_0	{ theor.	2.28	2.51	2.73	2.83
	{ emp.	2.09	2.58	2.77	2.98
U_0	{ theor.	-141.2	-130.9	-122.1	-119.0
	{ emp.	-148.1	-125.9	-120.7	-113.4
S	{ theor.	23.3	31.4	26.3	29.6
	{ emp.	30.2	26.4	24.9	24.0
w	{ theor.	2.35	2.33	2.29	2.28
	{ emp.	2.3	2.2	2.1	1.9
κ	{ theor.	15.9	22.6	31.0	35.1
κ emp.	{ extr. to $T=273^\circ$	16.2	41.7	33	54
	{ extr. to $T=0^\circ$	7.7	20.7	—	—

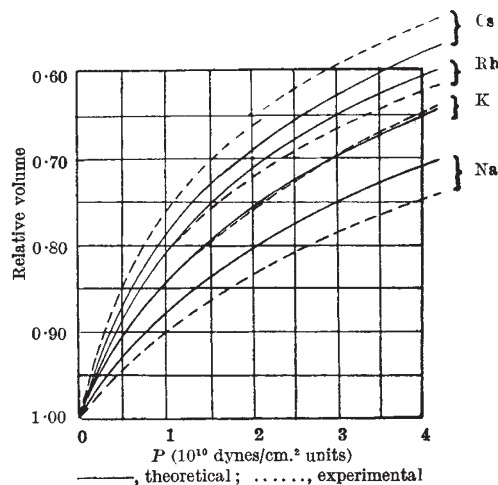
For the sake of comparison we have given in the table, besides the theoretical results, the corresponding experimental values. From the data we can see that the agreement between theoretical and empirical values is quite satisfactory. In the case of κ a direct comparison with experimental values cannot be carried out, because the calculations refer to the absolute zero of temperature whereas the measurements were performed at much higher temperatures. The real empirical values of κ at $T = 0^\circ$ lie between the values we get by linear extrapolation of the empirical values to $T = 0^\circ$ and $T = 273^\circ$. These values are given in the last two rows of the table in cases where the extrapolation could be carried out. As can be seen, we may expect that the theoretical values of κ will agree well with the empirical values at $T = 0^\circ$. The discrepancy between the theoretical and experimental values of w may have its origin in the circumstance that the double layer on the surface of the metals has been neglected throughout the computation of w .

With the help of the formula for U , we can derive the relation between the volume and the pressure at $T = 0^\circ$ by using the equation

$$P = -\frac{dU}{d\Omega} = -\frac{1}{4\pi R^2} \frac{dU}{dR},$$

where P denotes the pressure and Ω the volume of the elementary sphere. These results are in good accord with the experimental values found by Bridgman⁴. The agreement can be well seen in the accompanying figure.

The theoretical results can be further improved by using for the electron distribution of the metal ions the more accurate wave mechanical distribution of Hartree or Hartree and Fock instead of the statistical distribution. Using the Hartree-Fock distribution⁵,



we obtain for potassium, in the above-mentioned units: $R_0 = 2.59$, $U_0 = -127.0$, $S = 27.5$, $\kappa = 26.1$.

It is possible still further to improve this theory by the introduction of the field of the modified potential into the statistical model of metals. Thus for alkali metals the eigen-function for the distribution of the metal electrons can be quite easily determined, and one finds⁶ practically the same constant distribution which was assumed in the introduction of this article. For the alkaline earths similar computations are possible; the agreement between the theoretical results and the empirical data—as was to be expected—is not quite as good as for the alkali metals, but nevertheless it is still quite satisfactory. A more detailed presentation of the results will be published elsewhere.

¹ Compare especially Gombás, P., *Z. Phys.*, 99, 729 (1936); the other works are quoted in Gombás, P., *Z. Phys.*, 117, 322 (1941).
² Gombás, P., *Z. Phys.*, 118, 164 (1941); 119, 318 (1942).
³ Gombás, P., *Z. Phys.*, 119, 318 (1942). The limiting radius r_0 used there can be replaced here by the limiting radius of the statistical Thomas-Fermi-Dirac ions.
⁴ Bridgman, P. W., *Proc. Amer. Acad. Sci.*, 72, 207 (1938). Bardeen, J., *J. Chem. Phys.*, 6, 372 (1938).
⁵ Hartree, D. R., and Hartree, W., *Proc. Roy. Soc., A*, 166, 450 (1938).
⁶ Gombás, P., *Math. u. Naturwiss. Anz. d. Ung. Akad.*, 59, 125 (1940).

IMPERIAL CANCER RESEARCH FUND

REPORT FOR 1945-46

DR. W. E. GYE, director of the scientific work of the Imperial Cancer Research Fund, gives, in his report (Pp. 42. London: Royal College of Surgeons, 1946) for the year 1945-46, the good news that war-time difficulties are now being overcome and that projects contemplated in 1939 will soon be resumed. During the War, important work has been done in the Fund's laboratories on the action of war gases on the eye. This included work on lesions caused by mustard gas and trials of British anti-lewisite (*BAL*) (see *Nature*, 156, 616; 1945). It is hoped that publication of results of studies of the action of other agents used in chemical warfare and of a general consideration of chemical injuries of the eye will be permitted in the future. The Fund's war work has shown that greater consideration should be given to the eye as an experimental medium.