

ON ATOMIC PROPERTIES WHICH MAKE
AN ELEMENT A METAL

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ABSTRACT

A criterion for determining when an element will show metallic conductivity.— From the dielectric constant of a gas or from its refractive index, extrapolated to long wave-lengths, the molar refractivity R can be calculated. In the solid or liquid state we have $(n^2-1)/(n^2+2) = Rd/M$. The left side cannot be larger than 1. If the right side becomes larger than 1, the dispersion electron is set free and the body then has metallic conductivity. The necessary and sufficient condition for metallic conductivity is therefore $R > M/d$. The prediction is verified in the case of metals for which the refractive index is known or for which it can be calculated. It is shown that the condition is probably satisfied in the case of metals for which the refractive index cannot be calculated with certainty. The conductivity of sodium dissolved in liquid ammonia is discussed.

FOR a transparent body the refractivity, $(n^2-1)/(n^2+2)$, is proportional to the density. That (n^2-1) does not vary proportionally with d is explained as follows. The polarization of a medium under the influence of an external electric force increases not only directly with increase in the number of molecules in unit volume, but also because of the presence of other polarized molecules near the one in question. These give rise to a force helping the external field, the so-called Lorentz-Lorenz force.

If p is the electric moment of a molecule and N the number of molecules per cm^3 , the polarization of 1 cm^3 will be

$$P = Np$$

The polarization of a molecule under the action of an electric force E is proportional to the force, thus $p = rE$ and we have for higher densities the equation

$$p = r(E + 4\pi P/3) \tag{1}$$

where the second term in the parenthesis is the Lorentz-Lorenz force. Writing N_L for the number of molecules in the mole, M for the molar weight and R for the molar refractivity, we have

$$4\pi N r = 4\pi N_L r d / M = 3Rd / M.$$

Since $4\pi P/E = n^2 - 1$, we get

$$n^2 - 1 = 3R \frac{d}{M} \left(1 + \frac{n^2 - 1}{3} \right) \tag{2}$$

or

$$(n^2 - 1)/(n^2 + 2) = Rd/M \tag{3}$$

As an example of the constancy of R we may recall that R for carbon disulfide vapor is 0.2805, while for the liquid it is 0.2898. The slight deviation of 3 percent between these two figures has to be explained by a real change in the molecule, a "deformation."¹ Of course the particular factor $\frac{1}{3}$ in Eq. (1) is valid only in isotropic or cubic substances.

Now it is quite clear that the value of the left side of Eq. (3) cannot be larger than 1. What happens, then, if we start with a substance of large refractive index in the gaseous state and compress it, increasing the value of Rd/M until it reaches 1? We may answer this question by considering the equation of motion of the dispersion electrons in the molecule according to the classical theory. In a single molecule this equation would be

$$m\ddot{p} + 4\pi^2 m\nu_0^2 p = e^2 f E$$

where ν_0 is the characteristic frequency in the free molecule and therefore a measure of the force holding the electron in the molecule; f is the number of dispersion electrons.

For higher densities the above equation must be replaced by

$$m\ddot{p} + 4\pi^2 m\nu_0^2 p = e^2 f (E + 4\pi P/3) = e^2 f (E + 4\pi N p/3)$$

or

$$m\ddot{p} + 4\pi^2 m\nu_0^2 (1 - Ne^2 f/3\pi m\nu_0^2) p = e^2 f E \quad (4)$$

Now we have

$$Ne^2 f/3\pi m\nu_0^2 = Rd/M \quad (5)$$

R being taken for infinitely long waves of incident light. Therefore the characteristic frequency of the electrons in the molecule is diminished to the value

$$\nu_0(1 - Rd/M)^{1/2}$$

If Rd/M is equal to 1 the resultant force on the electron vanishes; the electron is set free.*

We conclude that the necessary and sufficient condition for a substance to have metallic conduction in the liquid or solid state is the following; It must have such a high value of R (which can be found by measuring the index of refraction in the vapor state for infinitely long wave-lengths) that

$$R > M/d \quad (6)$$

if the density of the solid or liquid state is inserted. This applies only if the vapor is monatomic, the solid nearly cubic or the liquid also monatomic.

¹ K. Fajans and G. Joos, *Zeits. f. Physik* **23**, 1 (1924).

* If we have a thin gas with N molecules, each with one isotropically bound electron the system has $3N$ equal natural frequencies. Increase of the density increases the coupling, and this splits up the coincidence. We calculate the three equal lowest frequencies for which alone Equation 1 holds (homogeneous polarization). This mode of vibration is the only one excited by light waves.

TABLE I

Values of R and of M/d for certain elements.

The refractive index n is for the vapor at 0°C and 1 atm. The data for Na were taken from Wood's² paper, for the rare gases from the compilation of Herzfeld and Wolf,³ the rest from Cuthbertson's⁴ measurements.

Element	n	R	M/d (cm ³)	Element	n	R	M/d (cm ³)
Na	1.0041	61	23.6	He	1.0000347	0.518	27.4
Zn	1.00096	14.6	9.2	A	1.000278	4.15	27.8
Cd	1.00134	20.0	13	Kr	1.000418	6.25	38.4
Hg	1.00092	13.74	14.61 (liq.) 14.22 (sol.)	X	1.000682	10.2	37.3
S ₂	1.00100	16.42	31	P ₂	1.00120	17.9	26.6 (metal) 34 (white)
Se ₂	1.00153	22.84	33 (metal) 37 (glass)	As ₂	1.00155	23.1	26.2
Te ₂	1.00237	35.4	40.8				

How well this condition is satisfied is seen by referring to Table I in which are presented the calculated values of R and of M/d for a number of substances whose refractive indices in the gaseous state are known. Of these elements, four are metals with monatomic vapor, Na, Zn, Cd, and Hg. Of these only Na is cubic but we expect no large deviation on account of this fact. For Na, Zn and Cd the relation (6) is fulfilled. For solid Hg Rd/M is 0.965 and the metallic state, which demands that this quantity be greater than 1, can be accounted for by a real change in R , a "deformation" as in the case of CS₂. For liquid Hg the calculated value is 0.94 and the metallic state could be accounted for by a formation of molecules Hg₂, if the distance of the two atoms in the molecule were about $\frac{3}{4}$ of the apparent average distance.

For the rare gases in Table I R is less than M/d as we should expect since they are non-metallic. For the remaining elements listed in the table, which have diatomic molecules, the formula cannot be applied rigorously. If we assume that it can be applied the non-metallic nature would follow from the results. It is gratifying to note that Rd/M has the highest value for Te and As (0.87 and 0.88).

There are no other direct measurements for R except for the gases H₂, O₂, etc., for which it is well known that the value of Rd/M for the condensed state is less than 1. In other gases we could calculate R from the formula

$$R = \sum N e^2 f / 3 \pi m v_i^2 \quad (7)$$

if we knew the electron number f for each absorption line. This number determines the strength of the absorption line.

² R. W. Wood, Phil. Mag. **8**, 293 (1904). The density was calculated with the ratio of fringe shifts at 496 and 644°C, and the absolute value at 500°C given by Zisch, Zeits. f. Physik **8**, 137 (1922). This value was checked by theoretical calculation according to Eq. (5).

³ K. F. Herzfeld and K. L. Wolf, Ann. d. Physik **76**, 71 (1925).

⁴ C. Cuthbertson and E. P. Metcalf, Proc Roy. Soc. **A80**, 411 (1908); Phil. Trans. **207**, 135 (1906).

For Na it has been shown that the index of refraction of the vapor can be fairly well calculated by taking $f=1$ for both resonance lines (D lines) together and neglecting the others.⁵ We shall now assume the same to be true for the other alkali metals and for copper, silver and gold. The results of the calculations are presented in Table II and are interesting in the following respect. It may be suggested that the non-metallic character of an element is determined by its large energy of ionization, or in other words by the force which holds the electron in place, or by ν_0^2 . While this is true in general, the real determining factor is the ratio of this force to the density fd/M of the dispersion electrons in space. For example, the silver atom with a shell of 18 electrons⁶ holds its dispersion electron much more strongly than do the atoms of the alkali metals. If it had, in the solid state, the large molar volume of potassium (44.7) it would *not* be a metal. It is a metal in spite of the low value of R only because of its low molar volume. On the other hand if the rare gas xenon, with $R=10.2$, had in the solid state the low molar volume of copper, 7.1, it would be a metal.

TABLE II

Values of R and of M/d for certain metals. R is calculated by means of Eq. (7).

	Li	Na	K	Rb	Cu	Ag	Au
Resonance line λ :	6708	5890	7664	7800	3247	3280	2427
R :	81.5	62.7	107	110	18.95	19.4	10.7
M/d :	13	23.6	44.7	55.8	7.1	10.2	10.2

For other metals the calculation cannot be made with any certainty. We give in Table III after the symbol of the element the wave-length of the resonance line used,⁷ then the value of R calculated with only one electron contributing to the strength of the line and neglecting other lines, then the molar volume M/d , the minimum f necessary to make the element a metal if no other line contributes, and finally the total number of electrons in the last n_k group. It must be remarked that Kuhn⁸ found for the line 2768 in Tl a value for f of only 0.24, while for the other strong line, 3775, (which for $f=1$ would alone give R a value of 25.7) he found a value for f of but 0.1. With these values for f the two lines together would result in a value for R of but 5.58. So long as we do not know more of the absolute intensities of the absorption lines we cannot give decisive data for the metals listed in Table III.

In this connection we may remark that the condensation of carbon atoms to diamond must result in a marked change in the electron orbits, for otherwise, with the small molar volume of diamond (3.4) and with $f=2$, the diamond would be a metal even if the resonance line had a wave-length as short as 970A.

⁵ Chr. Fuchtbauer and W. Hofmann, Ann. d. Physik **43**, 96 (1914). R. Ladenburg and R. Minkowski, Zeits. f. Physik **6**, 153 (1921).

⁶ H. G. Grimm, Zeits. f. Phys. Chem. **98**, 359 (1921).

⁷ Taken from H. N. Russell, Astrophys. J. **61**, 223 (1925).

⁸ W. Kuhn, die Naturwiss. **13**, 725 (1925).

TABLE III

*Values of R and of M/d for certain metals.*R is calculated from Eq. (7) assuming $f=1$ for the single resonance line given in the second column.

Element	λ	$R(f=1)$	M/d	$f(\text{min})$	Electron number in last group
Be	2348	10.0	5.2	0.52	2
Mg	2852	14.7	14.1	0.96	2
Ca	4226	32.0	25.9	0.81	2
Sr	4607	38.4	34.5	0.90	2
Ba	5535	55.4	36	0.65	2
B	2498	11.3	4.5	0.4	1
Al	3961	29.3	10	0.34	1
Ga	4033	29.3	11.8	0.40	1
In	3256	19.1	16.1	0.84	1
Tl	2768	13.8	17.2	1.25	1
Pb	2833	14.5	18.25	1.26	2
Ti	3998	29.0	10.7	0.37	4
V	3841	26.6	9.28	0.35	5
Cr	4254	32.7	7.76	0.24	6
Mo	3902	27.6	10.65	0.39	6
Mn	4030	30.0	7.4	0.25	7
Fe	3720	25.9	7.1	0.27	8
Co	3465	21.6	6.8	0.31	9
Ni	2320	9.7	6.7	0.69	10
As	2349	10	13.1	1.31	3
Sb	2311	9.75	18.5	1.9	3
Bi	3067	17.0	21.5	1.27	3

It is well known that according to Kraus⁹ sodium dissolved in liquid ammonia is a conductor. If the molar conductivity is plotted against concentration it shows first for increasing concentration a decrease, as usual in electrolytes. But above 1 mole in 20 liters there is a slight increase and above 1 mole in 900 cm³ there is a strong increase in conductivity with concentration. From considerations similar to those already mentioned we should expect that in ammonia the valence electrons are set free by mutual action of neighboring sodium atoms at concentrations above 1 mole in 500 cm³, while for lower concentrations the conductivity would be due only to the action of ammonia on the sodium.

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⁹ C. A. Kraus, Jour. Am. Chem. Soc. **43**, 749 (1921).