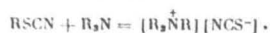


Tertiary amines react with organic thiocyanates as follows, regardless of the proportions of the components:



The symmetrical form of the conductivity isotherm, quoted by the above authors in connection with the ethyl thiocyanate-pyridine system, is seen by the present author as further evidence for this scheme. The sharp maximum at 50 mole % corresponds to the 1:1 ionic compound. Because of the low viscosity of mixtures of the system, their electrical conductivity isotherm does not have a minimum, as is often observed when interaction between components brings about a steep rise of viscosity³.

SUMMARY

1. In binary systems formed by benzyl thiocyanate with aniline, pyridine, and piperidine, two compounds in which the thiocyanate is combined with the amine in 1:1 and 1:2 ratios are formed, depending on the composition of the mixture.
2. Property-composition diagrams with singular points are obtained not only when the components interact completely to form one undissociated compound, but also when reaction is incomplete or in a system when two or more compounds are formed simultaneously.

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Lvov Medical Institute

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THE COMPRESSIBILITY OF METALS

V. V. Demchenko

The existing methods for the calculation of the compressibility of a metal, which are based on the Thomas-Fermi statistical model¹ or the electronic theory of metals², show satisfactory agreement with experimental data only for

alkali metals. The compressibility of a metal is believed to be due to the compressibility of the valence electrons of its atoms^{1,2}, that of the metal ions being practically zero^{1,2}. On this basis it is possible to obtain simply an approximate formula for the calculation of the compressibility of metals. We shall employ the concept of the volume V of the valence electrons, defined as the difference between the volume of the atom $V_a = (2R_a)^3$ and the volume of the ion $V_i = (2R_i)^3$:

$$V = 8(R_a^3 - R_i^3) \quad (1)$$

The concept of the volume of valence electrons has been used by a number of authors for the calculation of various properties of metals³⁻⁵.

We have the following expression for the pressure of valence electrons⁶:

$$p = \frac{(ze)^2}{2} \frac{d}{dV} (1/C), \quad (2)$$

where $e = 4.8 \times 10^{-10}$ CGSE, z is the number of valence electrons per atom, and C their capacitance, which for a given shape of an object⁹ is proportional to its linear dimensions⁶:

$$C = R = \frac{V^{1/3}}{2}. \quad (3)$$

Thus we obtain for the pressure

$$p = \frac{(ze)^2}{3} V^{-2/3}. \quad (4)$$

From Eqns. (4) and (1), we obtain the following final equation for the compressibility of a metal:

$$\kappa = -\frac{1}{V} \frac{dV}{dp} = \frac{36(R_a^3 - R_i^3)^{2/3}}{(ze)^2}. \quad (5)$$

Eqn. (5) shows that $\kappa = 0$ when $R_a = R_i$, *i.e.* the compressibility of the metal ions is zero. It is interesting that the electronic theory of metals and the Thomas-Fermi statistical model predict different modes of variation of κ with atomic radius: thus according to the first the compressibility is proportional to R_a^5 ,² and according to the second it is proportional to R_a^4 .¹ Eqn. (5) leads to a variation of κ with R_a similar to that derivable from the Thomas-Fermi model.

Eqn. (5) is approximate, but, as can be seen from the Table, it leads to satisfactory agreement with the experimental values of κ for a large number of metals. The Table compares the values of $\kappa \times 10^{12} \text{ bar}^{-1}$ calculated from Eqn. (5) with experimental data; a further comparison is made with κ for a number of metals derived on the basis of

Metal	κ (Ref. 5)	κ (expt.)	κ_1	κ_2	Metal	κ (Ref. 5)	κ (expt.)
Li	8.30	8.87	—	4.80	Zn	1.40	1.72
Na	16.30	15.90	10.40	13.30	Cd	1.63	2.30
K	37.60	37.50	24.20	37.80	Co	1.30	1.41
Rb	47.80	53.10	32.20	53.00	Sn	1.63	1.92
Cs	63.50	71.50	42.90	80.50	Pb	2.20	2.42
Mg	2.35	3.01	1.69	—	Fe	0.58	0.60
Ca	4.98	5.82	3.80	—	Ni	0.60	0.54
Sr	6.86	8.38	5.42	—	Mn	0.81	0.81
Ba	9.22	10.40	6.39	—	Cr	0.66	0.62
Be	0.63	0.79	—	—	Co	0.62	0.55