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

$$RSCN + R_3N = [R_3\overset{+}{N}R][NCS^-].$$

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 viscosity[5].

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.

1. S. P. Miskidzh'yan, Zhur. Obshch. Khim., 26, 1046 (1956); 27, 1755 (1957); 28, 276 (1958); Zhur. Fiz. Khim., 33, 1610 (1959); 33, 2002 (1959); 34, 157 (1960); 34, 802 (1960); 34, 2661 (1960) [Russ. J. Phys. Chem., 76 (1959); 257 (1959); 71 (1960); 382 (1960); 1253 (1960)]; S. S. Kirilyuk and S. P. Miskidzh'yan, Zhur. Fiz. Khim., 33, 1918 (1959); 33, 2786 (1959) [Russ. J. Phys. Chem., 220, 629 (1959), and others.
2. L. L. Konovalova and V. F. Ust'-Kachkintsev, Zhur. Obshch. Khim., 30, 246 (1960).
3. M. I. Usanovich and E. A. Bekturov, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 3, 837 (1960); 4, 374 (1961); 4, 574 (1961).
4. N. A. Menshutkin, Zhur. Russ. Fiz.-Khim. Obshch., 27, 137 (1895).
5. N. S. Kurnakov, "Sobranie Izbrannykh Rabot" (Selected Papers), Vol. 1, GONTI, 1939.
6. N. A. Trifonov, Izv. Permsk. Biol.-Nauch. Inst., 7 (1931).
7. I. N. Bachter, I. Cymerman, *et al.*, Chem. Zentr., 129, 4158 (1958); Yanogimoto, Referat. Zhur. Khim., No. 15, 46311 (1956).

Lvov Medical Institute Received 26th February 1962

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 model[1] or the electronic theory of metals[2], 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 metals[3-5].

We have the following expression for the pressure of valence electrons[6]:

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

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 object[9] is proportional to its linear dimensions[6]:

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

Thus we obtain for the pressure

$$p = \frac{(ze)^2}{3}V^{-5/3}. \quad (4)$$

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

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

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 $\kappa \times 10^{12}$ 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.)	$^*\kappa_1$	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	Ge	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