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.

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THE COMPRESSIBILITY OF METALS

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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 $V_i = (2R_i)^3$:

$$V = 8(R_a^3 - R_i^3). \tag{1}$$

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]:

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

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]:

$$C = R = \frac{V^{1/3}}{2}. \tag{3}$$

Thus we obtain for the pressure

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

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

$$\kappa = -\frac{1}{V}\frac{dV}{dp} = \frac{36(R_a^3 - R_i^3)^{4/3}}{(ze)^2}. \tag{5}$$

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

the Thomas–Fermi model[1] (denoted by κ_1) and the electronic theory of metals[2] (denoted by κ_2). The values of R_a and R_i used in the calculation were taken from Zhdanov[7], and the experimental values of κ were obtained from Ref.8. It was assumed that $z = 2$ in the case of all the metals except for the alkali metals which have $z = 1$. The calculation could not be made for many metals (W, Zr, Mo, Ta, Nb, Bi, Sb, etc.) because of the lack of data on the ionic radius with the given number ($z = 2$) of valence electrons.

I should like to acknowledge my great indebtedness to N.E.Khomutov for discussing this work.

SUMMARY

Using the concept of the volume of valence electrons, a formula has been derived for the compressibility of metals which is applicable to metals of various Groups of the Periodic System. The predicted variation of the compressibility with the atomic radius is similar to that obtainable from the Thomas–Fermi model.

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EFFECT OF ATOMIC COORDINATION ON THE TEMPERATURE VARIATION OF HEAT CAPACITY AT LOW TEMPERATURES

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It is known that the temperature variation of the heat capacity of various substances does not obey a single law. The form of the heat capacity curve of any substance depends on the properties of the chemical bond, the ratio of the masses of different atoms, and the crystal-chemical structure of the substance. The effect of structural peculiarities of such groups of substances as molecular, chain, and layer crystals on the temperature variation of heat capacity has been examined by Born[1] and Tarasov[2,3], who modified the Debye theory to take into account the specific features of the structure of the above crystals. The experimental heat capacity curves for these crystals exhibit a much greater deviation from the Debye theory than those for crystals with a continuous three-dimensional framework comprising identical chemical bonds. But even among the latter, although the majority do obey satisfactorily the Debye function, there are some which exhibit a pronounced deviation from it.

The aim of the present work is to show that the extent of deviation of the heat capacity curve for a crystal from the Debye function is largely determined by the magnitude of the atomic coordination with nearest neighbours. The problem is solved by comparing experimental low-temperature heat capacities and atomic coordinations of various substances. Before making this comparison, however, it is necessary to take into account the following consideration. The applicability of the Debye model (an isotropic elastic continuum) to a real crystal with a single type of bonding depends not only on the chemical bond but also on the ratio of the atomic masses and on the atomic coordination. In this respect the closest approach to an isotropic continuum is obtainable with structures having the maximum coordination with respect to nearest neighbours, *i.e.* having the closest packing with a coordination number of 12. Any decrease in the coordination number will therefore lead to an increase in the difference between the Debye model and the properties of a real crystal.

As will soon be made evident, the above postulate is in good agreement with experimental data for the heat capacities of a large number of crystals. It should be noted that the difference between experimental heat capacities at constant pressure and those at constant volume, to which the present theory applies, becomes substantial at relatively high temperatures. Therefore, to a first approximation, in comparing experimental data with the theory we shall set an upper limit to the reduced temperature, *i.e.* $T/\theta_D = 0.3$. In the Table the criterion reflecting the deviation of experimental heat capacities of substances having different atomic coordinations from the Debye theory, is the ratio of the maximum and minimum characteristic Debye temperatures, denoted by $\theta_{D_{max}}/\theta_{D_{min}}$. The values of this ratio for the substances listed in the first and second rows of the Table have been taken from Eucken's review[4] or calculated from the graphs in Blackman's review[5]. Those for SiO_2, GeO_2, and B_2O_3 have been calculated by the author from experimental data[6–8]. When a substance rigorously obeys the Debye law, $\theta_{D_{max}}/\theta_{D_{min}} = 1$.

Substances	C.N. or M.C.N.	$\theta_{D_{max}}/\theta_{D_{min}}$
Au, Pb, Na, K, Mo, Pt, Cu, Al, Ag, Fe, KCl, FeS_2, LiF, KBr, CaF_2	12—5.3	not more than 1.13
Ge, Si, Sn(grey), ZnS	4	1.43—1.6
SiO_2, GeO_2, B_2O_3	2.66—2.4	~2.17