OPTICAL PROPERTIES OF MIXED CRYSTALS.

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FORMULAE FOR MIXED CRYSTALS.

The object of a theory applicable to mixed bodies is to deduce the properties of the mixtures from the proportions and properties of the components.

Mallard[1] first proposed a theory for mixed crystals, offering for consideration two quite general methods of calculating optical properties of a mixed crystal from those of its components.

His results may be written thus for a cubic crystal:[2]

$$\left(\frac{1}{N}\right)^2 = m.\left(\frac{1}{n_1}\right)^2 + (1\text{-}m).\left(\frac{1}{n_2}\right)^2 \qquad (1a)$$

$$N = m.n_1 + (1\text{-}m).n_2 \qquad (1b)$$

For the three principal refractive indices of an orthorhombic crystal there appear three analogous equations.

The second formula (1b) is the same as Dufet[3] had obtained empirically. However, in discussing the related Gladstone law, Wulf[4] showed that the composition of the mixture should be expressed in percentage by volume instead of molecular percentage, but later he, and also Gossner,[5] concluded that there is no perfect linear relation.

FORMULAE FOR MIXED BODIES.

Since the time of Newton some function of the refraction that remains constant for different pressures and temperatures has been sought. Such a function has been called the specific

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[1] Mallard, E., various papers compiled in his Traité de Cristallographie 2, 1884. His theory depends on the analogy of the phenomena produced by the superposition of thin crystalline plates.

[2] Throughout the present paper the index of refraction of a mixed crystal will be marked N, and the indices of refraction of the components n_1 and n_2. In the same way the densities are marked D, d_1, and d_2, and the lattice constants A, a_1, and a_2, The mixed crystals contain m molecular per cent of the component n_1 and (1-m) molecular per cent of m_2; similarly w and v represent the weight and volume percentage respectively.

[3] Dufet, H., Bull. Soc. France Min. 1, 58, 1878. Compare also: A. Fock, Zeitschr. f. Kryst. 4, 583, 1880; and A. Lavenir, Bull. Soc. France Min. 17, 153, 1894.

[4] Wulf, G., Zeitschr. f. Kryst. 36, 1, 1902; 42, 558, 1907.

[5] Gossner, B., Zeitschr. f. Krist. 43, 130, 1907; 44, 417, 1908.

refraction and will be marked *k*. It has often been assumed that the specific refraction does not change its value if two or more bodies combine to a mixed body.

The first formula of the specific refraction has been given by Newton:

$$k = \frac{n^2 - 1}{d} \qquad (2a)$$

The law of Dale and Gladstone:

$$k = \frac{n - 1}{d} \qquad (2b)$$

was found empirically and corresponds to the formula introduced by Beer for gases. It was later replaced by a theoretical formula of Clausius-Mosotti and Lorentz-Lorenz:

$$k = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} \qquad (2c)$$

However, Wiener[6] showed that this formula nevertheless was objectionable from a theoretical point of view, and recently Lichtenecker[7] has set forth a fundamental new formula which depends on the constancy of the following expression:

$$k = \frac{\log n}{d} \qquad (2d_1)$$

By consideration of a change of the volumes this formula leads to the following equation:

$$\frac{1}{D} \cdot \log N = \frac{w}{d_1} \log n_1 + \frac{(1 - w)}{d_2} \log n_2 \qquad (2d_2)$$

It is obvious that if these formulae are to be tested on mixed crystals, it is necessary to know the volume relations of the mixed crystals.

THE VOLUME RELATIONS OF MIXED CRYSTALS.

Through very accurate determinations of the density of mixed crystals, Retgers[8] was able to state his well-known law, which can be written thus:

$$A^3 = m a_1{}^3 + (1-m) a_2{}^3 \qquad (3a)$$

From his X-ray measurements on mixed crystals of KCl and

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[6] Wiener, O., Die Theorie des Mischkörpers für das Feld der stationären Strömungen. Akad. Wiss. Abh. 52, 509, Leipzig, 1912.

[7] Lichtenecker, K., Physikal. Zeitschr. 27, 116; 833, 1926.

[8] Retgers, J. W., Zeitschr. f. physik. Chemie 3, 497, 1889.

KBr Vegard,[9] however, tried to show that the first power of the lattice spacing was proportional to the molecule percentage, thus:

$$A = ma_1 + (1\text{-}m)a_2 \qquad (3b)$$

Also the general lattice theory applies to this problem, and Grimm and Herzfeld[10] were able to show that the lattice spacings of a (cubic) mixed crystal can be computed theoretically from the following general equation:

$$A^v = m.a^v_1 + (1\text{-}m).a^v_2 \qquad (3c)$$

where $(v + 1)$ is the exponent of repulsion, defined through the minimal value of the potential energy.

Unfortunately the X-ray measurements are not so exact as to determine the exponent with any great accuracy, but nevertheless I think it is safe to say that the theoretical value of the exponent does not hold true in all cases. An example is furnished by the alkali halides, for which an exponent v about 8 should be expected.[11] But Grimm and Herzfeld themselves have shown that the heat of formation of a mixed crystal can be calculated with the help of the lattice theory of Born and Landé if the lattice spacings are known, and the calculated values of the alkali halides are best matched by the observations if v is equal to 3.

Further, Havighurst, Mach, and Blake[12] have X-rayed several mixed crystals of the alkali halides. They found that in most cases the exponent was between 1 and 3. A discrimination between those two was impossible, whereas $v = 8$ was quite incompatible with the measurements.

Later several authors have tried to show experimentally that Vegard's additivity law holds true (equation 3b). Vegard[13] himself, however, has recently investigated systems to which this law does not apply, and in some cases it has been shown that no smooth curve can be drawn for the lattice constants.

It is thus obvious that the volume relations of mixed crys-

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[9] Vegard, L., Zeitschr. f. Physik. 5, 17, 1925.

[10] Grimm, H. G., and Herzfeld, A., Zeitschr. f. Physik. 16, 79, 1923.

[11] The repulsion exponent of the alkali halides has been found to lie between 7 and 10. Cf. M. Born, Fortschr. d. math. Wiss. 4, 2 Aufl. p. 735.

[12] Havighurst, R. J., Mach, E. and Blake, F. C., Jr., Journ. Am. Chem. Soc. 47, 29, 1925.

[13] Vegard, L., Vid. Akad. Skr.: I, No. 5, Oslo, 1927; Zeitschr. f. Krist. 67, 148, 1928. See also: A. E. van Arkel and J. Basart, Zeitschr. f. Krist. 68, 475, 1928.

tals are complicated, and that it is impossible to deduce the lattice spacings of a mixed crystal from those of its components.

Mixed Crystals of TlBr-TlI.

The system of TlBr-TlI forms a continuous series of mixed crystals with the CsCl-arrangement of their ions (body centered cube).

Only one modification of TlBr is known. The stable modification of TlI and of the mixed crystals rich in iodine has, however, an orthorhombic structure which at 175° C. (for pure TlI) inverts into the cubic form; but the cubic structure exists at ordinary temperature in a metastable condition for some days if the crystals are quickly cooled and carefully handled (shaking and grinding will cause inversion).

Accurate X-ray measurements of the lattice spacings of the mixed crystals are on record.[14] New data on refractive indices are given in Table I.

In Fig. 1 the relations between the lattice spacings and the composition is given. It is worth noticing that the curve for the spacings fits the theoretical equation of Grimm and Herzfeld for an exponent equal to 8.

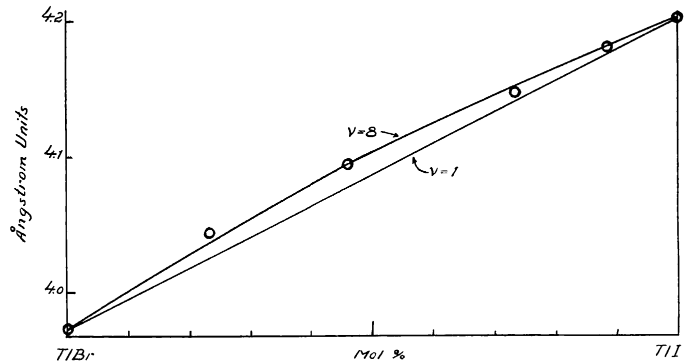

Fig. 1. The unit lattice spacings of the mixed crystals of TlBr-TlI. The curves are drawn according to the general equation of Grimm (3c) for an exponent $v = 8$ and $v = 1$.

In Fig. 2 the relation between the indices of refraction and

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[14] Barth, T., and Lunde, G., Zeitschr. physik. Chemie, 122, 299, 1926.
Lunde, G., Zeitschr. physik. Chemie, 117, 51, 1925.
Barth, T., idem. 131, 105, 1927.

the composition is given. It is obvious that none of the formulae of the optical properties hitherto given hold true.

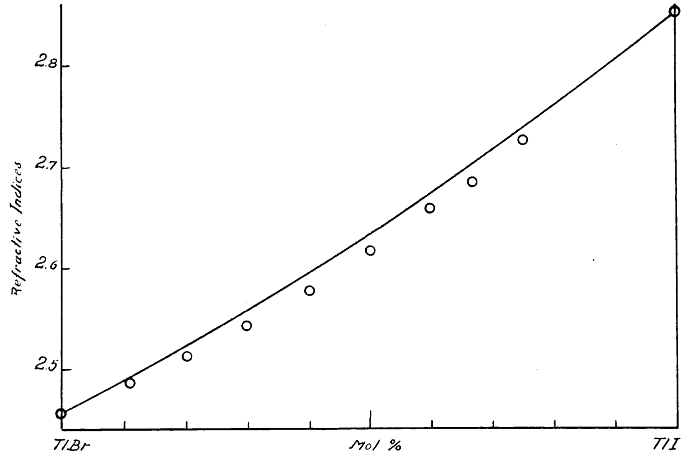

Fig. 2. The refractive indices of the mixed crystals of TlBr-TlI. The observations are marked with little circles. The curved line represents the theoretical values, calculated from Lorentz-Lorenz' formula (2c). If some of the other formulae for mixed bodies be used, the disagreement with the observed values is still greater.

Table I. Refractive Indices of the thallous halogenides.
(Caesium Chloride Structure)

Mol per cent		Refractive Indices					
				D	Hg	Hg	Hg
		.750μ	.650μ	.589μ	.578μ	.546μ	.436μ
TlCl		2.198	2.223	2.247	2.253	2.270	2.400
TlBr	TlI						
100	0	2.350	2.384	2.418	2.424	2.452	2.652
89	11					2.482	
80	20			2.468		2.511	
70	30		2.455			2.541	
60	40					2.578	
50	50		2.518		2.567	2.616	
40	60				2.615	2.660	
33	67					2.683	
25	75		2.610	2.662	2.673	2.722	
0	100		2.72±	2.78±		2.85±	

Mixed Crystals of AgBr-AgI.

The system AgBr-AgI is interesting because the end members have different structures. AgBr crystallizes in the sodium chloride arrangement, and AgI in the zinc sulphide (or zinc oxide) arrangement. As these modifications are overlapping in the mixed crystals these two substances are able to mix in all proportions, and thus they furnish an example of isodimorphism.

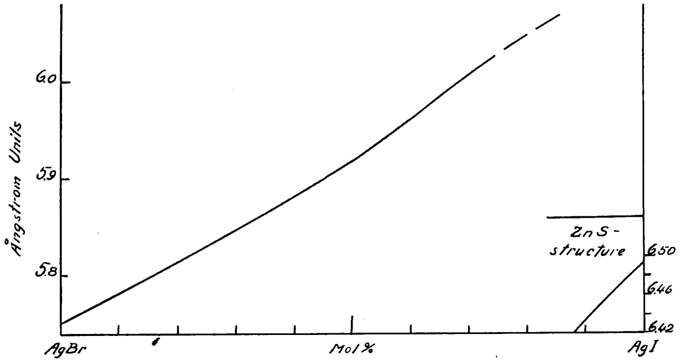

Fig. 3. The unit lattice spacings of mixed crystals of AgBr-AgI in the sodium chloride arrangement. To the right are shown the iodine rich crystals crystallizing in the diamond arrangement.

Isodimorphism is defined as the power of two substances to crystallize in two different, reciprocally isomorphous modifications. One of these modifications, however, is often unable to exist independently of the other at the temperature concerned, and is then only known in isomorphous mixtures.

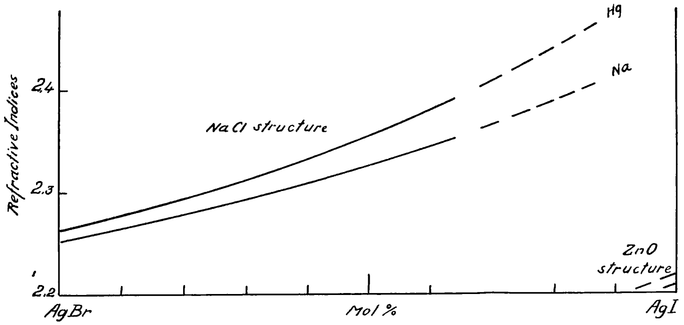

Fig. 4. The refractive indices of the mixed crystals of AgBr-AgI. For green mercury light (.546μ) and for sodium light (.589μ). To the right are shown the indices of the iodine rich, birefringent mixtures, crystallizing in the ZnO-structure.

In Fig. 3 the volume relations of this system are shown; and Fig. 4 shows the indices of refraction.[15] As the curve of the spacing and the curve of the refraction both are concave, it is impossible to bring them in agreement with any of the formulae for the optical properties of mixed bodies. The experimental data of the X-ray investigations will be found in the cited paper by Lunde and myself (Zeitschr. physik. Chemie 122, 293, 1926). New optical data are presented in Table II.

TABLE II. Mixed Crystals of AgBr and AgI.
(Sodium Chloride Structure)

Mol %		Refractive Indices			
		D	Hg	Hg	Hg
AgBr	AgI	.598μ	.578μ	.546μ	.436μ
100	0	2.252	2.256	2.263	2.363
67	33	2.299	2.303	2.320	
33	67	2.36±		2.40±	

Mixed Crystals of $BaO.2SiO_2$ and $2BaO.3SiO_2$.

A very interesting case of formation of mixed crystals has been studied by Eskola.[16] The compounds $BaO.2SiO_2$ and $2BaO.3SiO_2$ form a continuous series of orthorhombic mixed crystals. The indices of refraction of this series are shown in Fig. 5. The deviations from a straight line are very great. It is very difficult to imagine the mode of formation of the mixed crystals in this case and one probably has to conceive a mutual geometrical substitution of barium by oxygen.

However, in most cases it has been found that the refraction of mixed crystals varies approximately proportional to the composition. Such a proportionality indicates two things:

1. One or other of the three formulae for mixtures is followed (equations 2a, 2b, 2c), but the observations fail to distinguish between them.

2. Grimm's general volume equation (3c) is followed but the measurements are not so exact as to determine the expo-

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[15] As all the investigated salts melt without decomposition the refractive indices could be determined on prisms which were moulded between two pieces of quartz glass. Ordinary glass could not be used, for it often was necessary to chill the preparations in order to prevent inversion, and as the melting points of these salts partly lie above 500° C. ordinary glass will inevitably crack.

[16] Eskola, P., this Jour. 4, 331, 1922.

nent v; it is obvious that it must be about 3 (Retgers' law, equation 3a), but it may also be 1 (Vegard's law, equation 3b).

If the units of the crystalline edifice be regarded as rigid bodies one should expect the volumes of the mixed crystals to be an additive function of their components ($v = 3$). According to Herzfeld[17] however, in a close-packed lattice of rigid spheres the distances and not the volumes are additive. If now the exchangeable ions differ much in size a suitable packing will cause an exponent which at any rate has a smaller value than 3. But as similarity in size of the ions is a necessary condition of the formation of mixed crystals an exponent v about 3 ought to indicate a mutual substitution of the ions taking place without influencing the field of repulsion (Wirkungssphäre), i.e., the formation of mixed crystals takes place without deforming the ions.

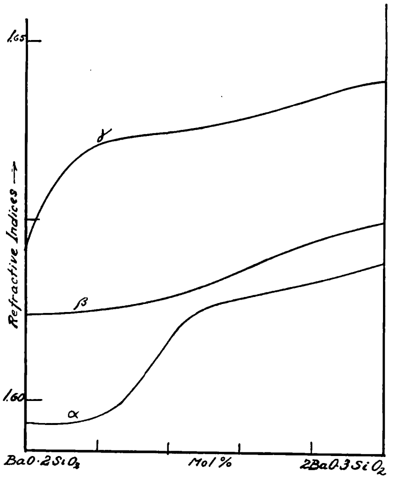

Fig. 5. The indices of refraction of mixed crystals of $BaO.2SiO_2$-$2BaO.$-$3SiO_2$ (Na-light), according to Eskola.

Such a mode of formation is apparently usually the case. It may, for example, be referred to several papers by Tutton,[18] who, attaching special weight to some very exact measure-

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[17] Kinetische Theorie der Wärme, p. 219, 1925; Geiger und Scheel, Handbuch der Physik. 22, 499 1926.

[18] Tutton, A. E. H., "Crystalline form and chemical constitution," 1926, p. 152.

ments by Porter,[19] strongly supports the view that the refractive indices, the directions of which are constant throughout a series of mixed crystals (i.e., if the indices are controlled by the crystallographic symmetry), will lie on a straight line.

THE CAUSES OF OBSERVED DEVIATIONS.

The question is now: Why do the systems TlBr-TlI and $BaO.2SiO_2$-$2BaO.3SiO_2$ show such great deviations from the proportionality of the refractive indices to the composition, whereas the other investigated series of mixed crystals usually show little or no deviations? The answer must be that the refractive power of a mixture not only depends upon its density, but also on the nature of the chemical bonds[20] and the degree of deformation of the ions.

As regards the case of the barium silicates it is easily understood that by a substitution of O by Ba in the lattice the surroundings of the atoms and the chemical bonds are changed.

In a mixed crystal of TlBr-TlI a great deformation of the anions has taken place. The only reason that TlI is able to crystallize in the CsCl-arrangement is because the iodine ions have got a great deformability and because the deforming action of the thallium ions is very strong.[21] This is also shown by calculating the specific refraction of these salts. The specific refraction:[22]

$$k = \frac{n-1}{d}$$

is related to the mole refraction: $R = k.M$ ($M =$ molecular weight) and, as the mole refraction may be taken as a measure of the polarisability of the ions,[23] it is worth noticing that the specific refraction of the halogen ions in this case is unusually high. Also the insolubility and the colors of these salts may be taken as indicative of ionic deformation.

The conclusion must consequently be the same as that which Spangenberg[24] arrived at through his studies of the alkali halides, that the specific refraction of an ion depends upon the surroundings.

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[19] Porter, M. W., Proc. Royal Soc., A. 109, 78, 1925.

[20] This corresponds to the well-known exaltation of organic chemistry.

[21] Cf. Goldschmidt, V. M., Geochem. Verteil.-Gesetze VII, p. 16. Vid. Akad. Skr. I, No. 8, Oslo, 1926.

[22] Gladstone's formula is used because of its greater simplicity.

[23] Pauling, L. Proc. Royal Soc. A, 114, 181, 1927.

[24] Spangenberg, K., Zeitschr. f. Krist. 53, 494, 1923.

	k obs.	k calc.
TlCl	.178	.149
TlBr	.188	.146
TlI	.244	.160

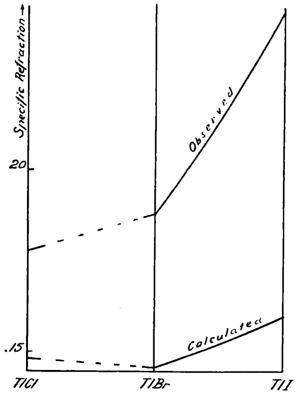

Fig. 6. The specific refraction, $\frac{n-1}{d} = k$, of the thallous halides. (Na-light.) The second column of the table gives the observed values, the third column the values calculated from the commonly used figures:

$k_{Cl} = .303$, $k_{Br} = .214$, $k_{I} = .226$, $k_{Tl} = .12$.

If one puts $k_{Tl} = .155$, a value which certainly is too high, the calculated refraction of TlCl agrees with the observation. But still the observed values of TlBr and TlI are respectively 10 and 30% higher than the calculations.

CONCLUSION.

It may therefore be concluded that if the formation of mixed crystals takes place without any deformation of the anions and without any changes of the chemical bonds, the refractive indices of the mixtures will vary approximately proportionally to the composition (excepting triclinic and, partly, monoclinic crystals).

If on the other hand such deformations or changes take place the deviations from this law will be the greater the greater the changes.

BEARING ON OPTICAL MINERALOGY.

One object of optical mineralogy is to determine the refractive indices of all minerals. As the most important minerals met with are mixed crystals, it is very significant to know the variation of the indices with the composition. In many cases, however, it has been taken for granted by mineralogists that the variations are rectilinear. This is not justified. The indices vary continuously, but not always proportionally to the composition.

Taking such a commonplace case as the amphibole group. According to Warren,[25] who recently has worked out the structure of the amphiboles, the unit cell of tremolite can be written $H_2Ca_2Mg_5Si_8O_{24}$, and in the common hornblende a mutual substitution *inter alia* of Al for Si is possible. By the formation of mixed crystals, say of actinolitic hornblendes this substitution takes place, the chemical bonds are changed, and it is therefore not to be expected that the refractive indices of these crystals will vary proportionally with the composition.

Another example is furnished by the natural nephelines, which can be regarded as mixtures of the nepheline silicate with kaliophilite, albite, and anorthite. There are reasons for believing that ω, the ordinary refractive index of nepheline, is but little affected by the content of anorthite. Because of this I have plotted the observed value of the index of the ordinary ray in the three component system nepheline-kaliophilite-albite, disregarding the anorthite constituent.[26]

The results arrived at are given in Fig. 7.

It is seen that the mixed crystals of $NaAlSiO_4$-$KAlSiO_4$ have higher refractive indices than any of the constituents.

One has to picture the formation of these mixed crystals by imagining a partial substitution of sodium atoms by potassium atoms. As the much larger K-atoms are forced into the lattice of $NaAlSiO_4$ the anions will be deformed until eventually their limit of deformability is reached, where it becomes impossible to force any more K-atoms into the lattice, i.e., the limit of the miscibility is reached (at about 30-40% $KAlSiO_4$).

It is thus very reasonable that the variation of the indices will appear as curved lines, as actually has been found.

Also in other mineral systems similar conditions occur, and in accordance with this Winchell[27] has drawn curved lines

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[25] Warren, B. E., Zeitschr. f. Krist. 72, 42, 1929.

[26] See for further references: T. Barth, Vid. Akad. Skr. I, No. 8, Oslo, 1927.

[27] Winchell, A. N., Am. Mineralogist 9, 108, 1924; this Jour. 11, 283, 1926. More data are compiled in his "Optical Mineralogy," N. Y., 1927.

for the optical properties of some of the recently investigated mineral systems, e.g., in the scapolite and chlorite groups, etc.

In mineral systems with a mutual substitution of atoms (ions) of the same valency and of approximately the same radius, the variation of the optical properties will be approximately proportional to the composition (e.g., diopside-hedenbergite, where Mg and Fe substitute for each other).

On the other hand, if ions (atoms) of different valency or size substitute for each other the optical properties have to be expressed as curved lines.

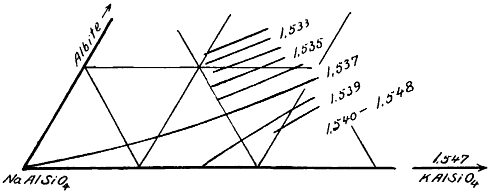

Fig. 7. The values of ω, the ordinary index of refraction of the system $NaAlSiO_4$-$KAlSiO_4$-$NaAlSi_3O_8$.

ACKNOWLEDGMENT.

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