SOLID SOLUTIONS[1]

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This is the fifth time that I have outlined the state of our knowledge of solid solutions and my views on this subject, at different periods of its development. The first time was twenty-two years ago, when, following a suggestion of van't Hoff, I wrote a pamphlet "Ueber feste Lösung."[2] In 1906 I delivered a lecture at the Sixth International Congress of Applied Chemistry in Rome,[3] which was followed by a discussion in which a prominent part was played by my lamented friend Richard Abegg. Two years later another lecture delivered at Breslau, upon the initiative of Abegg, gave rise to a little book.[4] Finally in 1912 I presented to the Accademia dei Lincei in Rome a monograph[5] in which my own researches and those of my coworkers were summarized. In the following pages these four papers will, for convenience, be referred to as Bruni I, II, III, and IV.

When today I again take up the matter and look around to survey the field, how changed I find it, how many advances have been made to which I have been a stranger! I refer chiefly to the epoch-making discovery of Laue which established beyond discussion the reality of the atomic lattice in crystals and gave to the crystallagrapher and chemist a tool never dreamed of before, and its practical application by the experimental methods

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[1] An essay prepared in connection with the dedication of the Sterling Chemistry Laboratory of Yale University.

[2] Published in the Ahren's *Sammlung chemischer und chemisch-technischer Vorträge* Band VI, 1901.

[3] Sixth Intern. Congress App. Chem. (Rome) **6**, 103–120 (1906).

[4] "Feste Lösungen und Isomorphismus" (Akadem, Verlagsgesellsch., Leipzig, 1908).

[5] Bruni, Memorie R. Accad. Lincei, Rome, **9** (1912), pp. 40–116.

worked out by the Braggs, by Debye and by Hull. Secondly, I will consider the indefatigable work of Tammann on the properties of mixed crystals of metallic alloys, their behavior toward physical and chemical agents and their so-called limits of resistance. Finally I meet the new and attractive theories as to the constitution of atoms and molecules, developed largely on this side of the ocean by Gilbert N. Lewis and by Irving Langmuir, which throw much light on the intimate structure of crystals.

I hope to be pardoned if I give to the following exposition a rather personal and historical turn. There are reasons for doing so. The later investigators very often seem not to possess a complete or extensive knowledge of the earlier literature of the subject. Nor can this arouse much surprise, for this literature already forms such an enormous mass that very few, if any, are able to master the whole of it. The perusal of old papers appears often unnecessary, and yet one might, even now, find in them, together with much that was transient and is now superseded, facts and ideas that would cause surprise and things that one might think to have discovered just now, under other conditions.

The results of physico-chemical researches are not always appreciated or understood by crystallographers of the old school, and conversely much of the strictly crystallographical work is little known to physico-chemists, and this lack of reciprocal knowledge has led to much confusion. Sometimes we do not speak at all the same language. Who among the modern physico-chemical students of isomorphism has really read throughout the papers of that genial, although too dogmatic, Dutch crystallographer, Retgers? And who has thoroughly perused that fascinating, although confusing, book "Physikalisch Chemie der Krystalle" of Arzruni, an inexhaustible mine of data and valuable hints? The work of still earlier authors, too, offers many points of interest. In a totally forgotten paper by an almost forgotten Italian chemist, Selmi,[6] published in 1844, on the so-called "chloroiodides of mercury," one finds

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[6] F. Selmi, "Studii sperimentali e teorici di Chimica molecolare" (Parma), 1844.

discussions concerning mixed crystals and chemical compounds that would not be wholly out of place in a paper by Tammann today.

In a recent very interesting paper on "The Nature of solid Solutions"[7] to which I shall return, Bain says, "English speaking scientists have chosen the word "solid solutions" to denote the specific state of association of two or more substances entirely homogeneous in the solid" and expands upon the "points of merit" of this expression in opposition to the German "Mischkrystalle." I am sure that Bain did not really mean what would be the literal sense of this phrase. But as it might be misleading to many readers of a widely circulated technical paper, who are not acquainted with the history of the subject, I hope to be excused if I linger a little upon this point. The expression "solid solution" and "solid solvent" seems to have been used for the first time by Lecoq de Boisbaudran in two papers presented in 1866 to the Académie des Sciences of Paris but not accepted by this illustrious body because it contained too revolutionary ideas. At any rate an abridged exposition of his views was not published until 1891,[8] a year and a half after the fundamental paper by van't Hoff.[9] In the course of his researches on fluorescence, published between 1886 and 1890,[10] Boisbaudran remarked that this property is scarcely shown by pure oxides, although it is very strong in mixtures, especially in dilute ones, and in this connection he spoke of "solid solvents." But this notion was not developed by him nor connected with other facts. The origin of this notion, belongs, without doubt, to the great Dutch physico-chemist, who a third of a century ago expounded the theory of solid solutions as an extension of his general theory of dilute solutions.

Bain points out that the name "solid solution" has "points of merit, even though in some respects the properties of solutions are not apparent." And points of merit it really has. First

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[7] E. C. Bain, *Chem. & Met. Eng.*, **28**, 21 (1923).

[8] Boisbaudran, *Compt. rend.*, **113**, 832 (1891); compare his claim for priority **142**, 195 (1906).

[9] van't Hoff, *Z. physik. Chem.* **5**, 322 (1890).

[10] See many papers *in Compt. rend.*

of all it had a distinct psychological advantage, for that name which was like a shock to the accepted notions of chemists and physicists aroused great interest and gave origin sometimes to angry discussions which the inoffensive expression "mixed crystals" would have failed to awaken. These discussions led to a thorough investigation of this domain, the knowledge of which was thus greatly advanced. It now seems hardly possible to dispute that such a name is justified. As Bain rightly puts it. "The fact that such solids are capable of a considerable change in constitution and temperature without entailing any phase change urges to this name." In fact, if solutions are to be defined as homogeneous bodies whose composition is capable of continuous variation, at least within certain limits, this definition is independent of the state of aggregation and is as applicable to solids as to liquids. Of course the term "homogeneous" may leave room for discussion, and it would be possible to give to this term such definition as would exclude solid solutions from the fine society of homogeneous bodies. If taken in the strictest sense of the work, not even the atom itself might be termed homogeneous today. The best definition seems to be given by Barlow[11] and accepted by Bragg[12] and by Tutton,[13] namely, that "a homogeneous structure is one, every point within which, if we regard the structure as without boundaries, has corresponding to it an infinitude of other points whose situations in the structure are precisely similar." Mixed crystals, when equilibrium is reached, correspond fully to this definition. Even the fact that the formation of solid solutions may be considered as due to homopolar affinities between the components, and that the mixed crystals may thus be regarded as a sort of loose compound, fails to establish a difference between solid and liquid solutions, since solubility in liquids is generally admitted to be due to the formation of solvates.

Of course miscibility in the solid state is subject to more restrictions than in the liquid state because a somewhat closer

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[11] Barlow, *Mining Mag.* **11,** 119 (1895).

[12] Bragg, *J. Chem. Soc.*, **121,** 2766 (1922).

[13] Tutton, *Ann. Reports* **19,** 234 (1922).

likeness of crystalline structure is required; but it is by no means rare. It is surprising that such a celebrated scientist as Arrhenius[14] thought it right to state that solid solutions are "rare occurrences," so that they may be neglected in the deductions of the laws of stoichiometry. Formation of solid solutions is really not so frequent at ordinary (i.e., low) temperatures, but the majority of metal alloys contain mixed crystals, and if we consider minerals it may be said that not solid solutions, but pure crystals are of rather rare occurrence.

DIFFUSION IN THE SOLID STATE

When we now proceed to consider the propriety of applying the laws of solutions to solid solutions and the extent to which such application may be carried, the first and most important point to be established is that of the existence of diffusion in the solid crystalline state. When van't Hoff announced his theory of solid solutions, the known examples of diffusion is the solid state were very few, and he was obliged to rely chiefly on diffusion in amorphous solids. The constitution of the latter however is so entirely different, that I prefer to confine myself, in the following pages, to diffusion in crystalline phases. Shortly after the publication of van't Hoff's paper the researches of Spring[15] on diffusion of zinc and cadmium in copper, and those of Roberts Austen[16] on that of lead in gold were published. But some of these cases are open to objection, namely, the best studied of them, that of lead in gold, because the two metals form definite compounds, and not mixed crystals. This led me to take up again experimentally the question of diffusion in metallic alloys, limiting myself to pairs which form solid solutions but no intermetallic compounds.

The researches, carried out in collaboration with Meneghini,[17] were on the systems Ni-Cu, Cu-Au, Ag-Cu. We deposited, by electrolysis, a layer of the first metal on the second and estab-

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[14] Arrhenius, *"Theorien der Chemie"* (Leipzig), 1906, p. 36–37.

[15] Spring, *Z. physik. Chem.* **15**, 73 (1894).

[16] Roberts Austen, *Trans. Roy. Soc., London,* **A187**, 409 (1896).

[17] Bruni and Meneghini, *Atti accad. Lincei,* (I) **20**, 671, 927 (1911).

lished gradual formation of the solid solution by measuring the electrical conductance of the wire; for as is well known, the conductivity of solid solutions is much smaller than that of a mechanical mixture of the two metals. In fact, after heating respectively at 1000°, 900°, and 800° for several hours the conductance sank to the value corresponding to the solid solution. We then tried to shorten the time of diffusion by increasing the contact surface, and prepared by electrolytic deposition a wire of 60 alternate layers of nickel and copper; in this case we succeeded in bringing about complete diffusion in 2 hours at 1000° as compared with 135 hours in the first experiment. This compound wire showed marked diffusion even at 500°. Finally we increased much further the fineness of the single layers. As these last experiments were described only in my last nomograph[18] which appeared in a periodical not widely circulated, the results seem to have remained practically unknown; so I think it best to give them here in some detail.

Starting from copper wires of 0.02 mm. diameter and by alternately and rapidly immersing them as cathodes in nickel and copper baths, we built up two wires consisting each of 560 alternate layers, and having an average final diameter of 0.25 mm. The resistance, as measured on a length of 25 mm. at room temperature was as follows:

Wire I—contained 59 per cent Cu

	Ohm
Initial resistance	0.285
After 3 hours at 200°C	0.315
After 22 hours at 200°C	0.365
After further 22 hours at 400°	0.860
After 44 hours at 400°	1.632

Wire II—contained 57.8 per cent Cu

	Ohm
Initial resistance	0.270
After 6 hours at 100°C	0.285
After 27 hours at 100°C	0.308
After further 15 hours at 300°	0.430
After further 22 hours at 400°	1.430
After further 9 hours at 550°	1.580

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[18] Bruni, IV, page 62–63.

In both cases the last value remained unchanged on further heating for many hours, so that evidently equilibrium was reached under these conditions. A third similar wire, consisting of 540 layers, was varnished to prevent oxidation and left to itself at room temperature. After a year its resistance (0.210 ohm at 19.8°) remained practically unchanged. It will be seen that diffusion is not noticeable at room temperature, but becomes quite appreciable at 100°, and at 400° is already so large that equilibrium may be reached in about two days.

Among recent researches on diffusion in metallic alloys that of Fraenkel and Houben[19] may be cited. They studied the system Ag-Au at 870° and ascertained the rate of diffusion, employing as a criterion the technique of Tammann on the limits of resistance to the action of ammonium sulfide. Although the method is not very sensitive they succeeded in demonstrating that diffusion proceeds according to the classical laws of isotropic diffusion. The diffusion coefficient of Au in Ag at 870° is 0.000037 cm^2/day. These results were confirmed recently by Weiss and Henry[20] who used the same method at 935°, 885°, and 835° for periods of 2 to 32 days; they found that the inverse of the time of diffusion varies exponentially with the temperature, so that the time interval for reaching a certain state is doubled by a lowering of 50°. We may cite also the work of Sirovich and Cartoceti[21] who studied the "cementation" of copper with powdered binary alloys, e.g., iron-manganese, chromium-manganese, and iron-aluminum; they found that the two metals penetrate at a very different rate—for example, while manganese diffuses fairly rapidly, iron practically does not enter at all.

Broadly speaking, diffusion between metals has been carefully studied. To explain the mechanism Rosenhain[22] has recently put forward the theory of "intercrystalline slip." He points

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[19] Fraenkel and Houben, *Z. anorg. allgem. Chem.* **116,** 1 (1921).

[20] Weiss and Henry, *Compt. rend.* **175,** 1402 (1922).

[21] Sirovich and Cartoceti, *Gazz. chim. ital.,* **51,** II, 245 (1921); **52,** I, 436 (1922); **52,** II, 233, 245 (1922).

[22] Rosenhain, *Chem. Met. Eng.,* **28,** 442 (1923).

out the well known fact that a really homogeneous solid is not formed on cooling a molten alloy, and the occurence of "cored" crystals is universal. But equalization takes place easily upon annealing. He believes that intense local forces set up in the immediate neighborhood of "stranger" atoms will cause slight slips, probably of only a few atom-diameters; probably only a row or single line of atoms will move, rather than a whole layer, but this would be sufficient to account completely for diffusion. According to this theory the "stranger" atoms which distort the lattice most would cause the most of this local slipping and diffuse fastest. To support this view he says that "the extremely sluggish diffusion in copper-nickel alloys has been noticed and in this we have seen that the lattice distortion is very slight." Here Rosenhain evidently ignores my studies cited above, or else he would not have spoken of the "extremely sluggish diffusion," since I have proved that it can be very fast. Furthermore, a theory of inter-metallic diffusion must explain not only the equalization of unequal distributions of solid solutions as crystallized from a molten mixture, but also the diffusion and formation of solid solutions starting from pure solid metals. In the last case when the two metals have *ab initio* only a contact surface in common it seems difficult to attribute the diffusion to forces set up by the distortion of the lattice by "stranger" atoms. However I think the assumption of slip as outlined by Rosenhain may be accepted, by admitting that it can be brought about also by the homopolar attractions between the two kinds of metallic atoms.

The so-called "cementations" occupy a place apart among metallic diffusions. The well-known process of carburation of iron from the surface is an example of this type of diffusion. The difference between these cases and those considered above is that between the two kinds of matter there is here only a loose contact, and that the penetration is probably to be considered as due not to a real diffusion in the solid state, but to the action of vapors of the cementing agent. That the cementation of steel may be brought about by gases and vapors of carbon compounds is well known; this matter has been studied with great success by Giolitti.[23] Recently Runge[24] has again studied this phenomenon, starting from electrolytic iron, with benzene, toluene, etc., as the "cementing" agents and using the measurement of the conductance as index of the progress of penetration; he does not however think fit to note that this procedure had been introduced by myself. The penetration follows the law of diffusion, a fact that had already been established forty years before by Colson.[25] Tammann and Schönert[26] have lately compared the diffusion of carbon into iron and into other metals. They found that while in the first case it is appreciable even at 750°, with other metals it is scarcely noticeable under 900°. The difference between "cementations" and real diffusions has been pointed out by Sirovich and Cartoceti, who emphasize, in their work referred to above, the influence of the vapor pressure of the migrating substance.

It is to be expected that the tendency to diffuse shall be maximal in monoatomic (metallic) lattices and will gradually decrease with increasing complexity of the molecule and of the lattice. Diffusion between non-metallic transparent crystals is of less frequent occurrence and has been much less studied, nay, its existence has been denied.[27] Particular stress has been laid on the occurrence among minerals of crystals consisting of layers of two isomorphous substances of different color or appearance, the contact surfaces of which are still absolutely sharp without trace of interpenetration, although they subsisted through geological epochs and some of them are supposed to have been formed at comparatively high temperatures. But the bearing of this argument ought not to be exaggerated, for it is to be remembered that such cases are observed in large crystals where the contact surface is comparatively very small. Experimental researches on diffusion between crystalline salts are very scarce. The first were those by myself and Mene-

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[23] Giolitti, "*La cementazione dell'acciajo,*" (Milano), 1912.

[24] Runge, *Z. anorg. allgem. Chem.* **115,** 293 (1921).

[25] Colson, *Compt. rend.* **93,** 1074 (1881); **94,** 26 (1882).

[26] Tammann and Schönert, *Z. anorg. allgem. Chem.,* **122,** 27 (1922).

[27] Bodländer, *Neues Jahrb. Mineral. Geol.* **12,** 52 (1898).

ghini[28] on the system KCl + NaCl. As these results seem to have remained totally unknown, for the reasons stated above, I shall give them here in some detail.

It is known that the two salts give a continuous series of mixed crystals when their molten mixtures are solidified, and that these solid solutions decompose on cooling. The solidification diagram is a continuous curve, with a minimum at 664° for the equimolecular mixture; the decomposition point of the last lies at 405°. The mixed crystals can be brought to, and preserved at, room temperature by quenching them. They may be distinguished from the mechanical mixture of the single salts by the heat of solution in water which amounts to 3600 cal. for an equimolal solution compared to 5700 cal. for an equimolal mechanical mixture. This property was used by us as an index of the progress of diffusion.

A first series of experiments was made by heating at 600°, i.e., 64° lower than the lowest possible melting point, portions of the aforesaid equimolal mixture. Then they were quenched and the heat of solution was measured with the following results:

	Calories
Before heating	5,720
After 2 hours at 600°	4,029
After 14 hours at 600°	3,954

The rate of diffusion may be termed an enormous one, since equilibrium is almost complete in 2 hours. A similar experiment, carried out at 500°, yielded the following values:

	Calories
After 5 hours at 500°	5,739
After 24 hours at 500°	5,173
After 30 hours at 500°	4,910

The rate of diffusion is here much lower, as is to be expected, but still quite marked. We then tried to increase the speed by augmenting the degree of dispersion of the solid mechanical mixture. This can be done by two procedures, both of which were tried:

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[28] Bruni, IV p. 50–63; Bruni and Meneghini, *Atti ist. Veneto,* **71,** II, 195 (1911).

1. If a molten mixture is cooled very slowly after solidification, so that the mixed crystals are decomposed, a much more intimate mixture is obtained than by simply grinding the two salts together.

2. A still better result is to be expected if molten mixtures are quenched soon after solidification, so as to bring the solid solutions to room temperature and are then left to themselves for a long time.

A certain amount of the mechanical mixture $KCl + NaCl$ was divided into two portions A and B. A was left unaltered, B was melted, solidified and then cooled very slowly. The solution heat of A was 5715 cal., that of B was 5590 cal., so that under these conditions the decomposition of the solid solution in B is almost complete. Both portions were now heated at 500° for 24 hours, quenched and pulverized; after that the solution heat of A was 5172 cal., and of B was 4768 cal. It will be seen that the lowering of the heat of solution and, thus the diffusion in B was almost double that in A, as was expected.

A third portion C was melted, quenched and left to itself. After 11 days the heat of solution was 5525 cal., indicating that the destruction of the mixed crystals was almost completed. But after heating for only 4 hours to 500° the heat of solution sank to 4222 cal., i.e., the diffusion had been enormously more rapid than in both A and B, according to our prediction.

Some years later my former pupil, E. Quercigh[29] experimented on the system $HgBr_2 + HgI_2$. The first salt, as is known from the researches of Reinders[30] gives mixed crystals with the β-form (yellow) of HgI_2. By simply grinding the two salts together and leaving them at room temperature (20°) for 24 hours he was able to observe the change of color characteristic of the formation of mixed crystals. This observation seems also to have remained unknown, since Tammann reports recently,[31] that a mixture of $HgBr_2$ and HgI_2 appeared unchanged after 60 days. I am unable to account for this discrepancy. At any

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[29] Quercigh, *Atti accad. sci. Napoli,* (2) **16,** Nr. 7 (1914).

[30] Reinders, *Z. physik. Chem.* **32,** 558 (1900).

[31] Tammann, *Z. anorg. allgem. Chem.* **107,** 200 (1919).

rate I can confirm the results of Quercigh, having myself observed with the microscope the same phenomenon. Quercigh, observed under the same conditions a rapid diffusion between AgI and CuI, and was thus able to explain the natural formation of the mineral miernite, which is a solid solution of both, from the pure iodides, iodyrite and marshite.

Tammann found a slight diffusion between $KClO_4$ and $KMnO_4$ and between $Na_2SO_4 \cdot 10H_2O$ and $Na_2CrO_4 \cdot 10H_2O$, but in the last named case the influence of moisture coming from the water of crystallization may be supposed to influence the experiment. On the other hand he observed no diffusion between $MgSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 7H_2O$. At any rate my researches prove that diffusion takes place between crystalline transparent salts and that the velocity of this process can be very great, even at a considerable distance from their melting point.

The recent observations by Vegard[32] are very important. He investigated, using the method of Debye and Hull, the X-ray spectra of mixed powders of two salts capable of giving solid solutions, such as $KCl +$ KBr, KCl and NH_4Cl, K_2SO_4 and $(NH_4)_2SO_4$. He found that when the mixture had not been finely ground together a superposition of both the single spectra was obtained, but after grinding them the spectra only of the mixed crystals appeared, but these lines were not sharp, which denoted that the mixed crystals thus formed were not homogeneous.

Very little is known as to diffusion in crystals of organic substances. Tammann investigated two pairs of isomorphous substances of which the one is colored and the other is colorless, namely, azobenzene with dibenzyl and stilbene and found an appreciable, although very slight, penetration.

We thus find that diffusion is easiest with monatomic molecules, i.e., with metals; following them come the binary salts like the alkali chlorides; the salts with more complex molecules and the organic substances show as expected increasing reluctance. We may however assume that it is not the whole molecule of one substance that is obliged to force its way into

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[32] Vegard, *Z. Physik.* **5**, 393 (1921).

the lattice of the other, but that the part of the molecule which is common to both remains in its place and that only the substituting atoms have to slip in opposite directions till equilibrium is reached. On this basis, in the systems KCl + NaCl at 500–600°, we believe that the chlorine lattice remains in place, only readjusting the unit distances, while the potassium and sodium ions slip one against the other. This view is supported by our knowledge of the mechanism of electrical conduction in solid electrolytes. It was already known that in amorphous solid electrolytes, such as silicates[33] only the cations migrate and it was believed that this was a general rule.[34] But the important work of Tubandt[35] has shown that this is not the case. Through a very ingenious device this investigator measured the transference number by the electrolysis of AgI, AgBr, AgCl, Ag_2S, Cu_2S, $PbCl_2$, PbF_2 in the crystalline state. He too found that only one species of ions migrate, but while in the five first named salts it is the cation Ag^+ or Cu^+ that moves, in the lead halides on the contrary it is the anion Cl^- or F^- that migrates. Thus one of the kinds of ions remains fixed and insures the stability of the lattice. When from this case we pass to the diffusion of azobenzene $C_6H_5 \cdot N=N \cdot C_6H_5$ and stilbene, $C_6H_5 \cdot CH=CH \cdot C_6H_5$, if we assume that the C_6H_5- groups of both substances remain in place, the groups $-N=N-$ and $-CH=CH-$ would have to be displaced reciprocally; such groups would encounter more resistance than the simple atomic groups.

HEAT OF FORMATION OF SOLID SOLUTIONS

A systematic study of this very important point has been made only for mixtures of alkali salts. The measurements of heat of solution in water of mixed crystals, compared with that of mechanical mixtures of the two single salts, furnishes as a difference the heat of formation of the solid solutions. The

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[33] Warburg and Tegetmeier, *Wied. Ann.* **21**, 622 (1884); **35**, 455 (1888); **41**, 18 (1890).

[34] See Tammann, *Z. anorg. allgem. Chem.* **118**, 95 (1921).

[35] Tubandt, *Z. anorg. allgem. Chem.* **115**, 105; **117**, 1 (1921).

following systems have been investigated; the value given is the heat of formation of an equimolal solid solution for the double molecule.

1.	$K_2SO_4-(NH_4)_2SO_4$	positive	Sommerfeld[36]
2.	$KClO_4-KMnO_4$	0 calories	Sommerfeld[36]
3.	$FeSO_4-CdSO_4$	(?) negative	Sommerfeld[36]
4.	KCl—NaCl	2100 calories	Kurnakow and Zemczucznj[37]
5.	KBr−NaBr	1400 calories	Kurnakow and Zemczucznj[37]
6.	KI−NaI	1250 calories	Kurnakow and Zemczucznj[37]
7.	KCl−RbCl	negative	Zemczucznj and Rambach[38]
8.	KCl−KBr	220 calories	Bruni and Amadori[39]
9.	KBr−KI	390 calories	Bruni and Amadori[39]
10.	KCl−KI	551 calories	Bruni and Amadori[39]
11.	$NaNO_3-NaNO_2$	400 calories	Bruni and Meneghini[40]
12.	$NaNO_3-KNO_3$	0 calories	Zawidzki and Schazzer,[41] Amadori[42]

It is seen that of the twelve cases studied nine gave negative values, two showed no appreciable heat of formation and one gave a (very small) positive figure. The last case seems dubious and a revision would be welcome. It is to be remarked that Sommerfeld worked with mixed crystals separated from mixed aqueous solutions, while in all other cases mixed crystals as separated from molten mixtures were used. It would be interesting to repeat Sommerfeld's experiments on mixed crystals of K_2SO_4 + $(NH_4)_2SO_4$ deposited in the last named manner.

At any rate we see that solid solutions are generally endothermic, i.e., their formation absorbs heat. This is quite in accordance with the fact that solubility in the solid state increases with the temperature. Further, if we consider the alkali halides, we see that the heat change is largest from the pairs KCl + NaCl, KBr + NaBr, KI + NaI, whose mixed crystals are formed by solidification but are destroyed upon cooling at room temperature. Then comes KCl + KI which

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[36] Sommerfeld, *Neues Jahrb. Mineral. Geol.*, **2,** 37 (1900); *Z. physik. Chem.* **36,** 754 (1901).

[37] Kurnakow and Zemczucznj, *Z. anorg. Chem.* **52,** 186 (1907).

[38] Zemczucznj and Rambach, *Z. anorg. Chem.* **65,** 403 (1910).

[39] Bruni and Amadori, *Atti ist. Veneto* **71,** II, 51 (1911).

[40] Bruni and Meneghini, *Gazz. chim. ital.*, **40,** II, 1 (1910).

[41] Zawidzki and Schazzer, *Kosmos,* **35,** 498 (1910).

[42] Amadori, *Atti inst. Veneto,* **72,** II, 451 (1912).

exhibits at room temperature a large gap from 7 to 90 per cent KCl in the series of solid solutions, while at the temperature of solidification this gap extends only from 49 to 91 per cent. The heat of formation of KBr + KI is somewhat less owing to the fact that the miscibility, complete at solidification, shows at 25° a gap between 34 to 93 per cent. Finally the smallest heat of formation within this series is shown by KCl + KBr where solubility in the solid state is complete in every condition. As far as experimental data are available we find that the larger the increase in solubility with the temperature, the larger is the heat of solution in the solid state, in accordance with what happens for the ordinary solubility. These facts seem not to have been considered, nor sometimes even known by recent authors. For example, Landrieu[43] speaks only of the work of Sommerfeld and ignores completely all the others above cited. He thus concludes that the heat of formation of mixed crystals is very near zero, a conclusion, as we have seen, entirely wrong.

Neither organic nor metallic solid solutions have been investigated from this point of view and it is desirable that they should be. Generally speaking it would be highly interesting to study the heat of formation in connection with the distortion of the space lattice of the single components. It would seem plausible that the amount of energy required to form the mixed lattice is a function of the degree of deformation involved in building it up.

CONSTITUTION OF SOLID SOLUTIONS

Scientists now possess an incomparable instrument for the investigation of this fundamental question in X-ray photographs taken by the three methods of Laue, Bragg, Hull and Debye. It is thus possible to ascertain the configuration of the space lattice and the dimension of its units, and to locate the situation in it of the individual atoms. The researches based upon these methods have demonstrated beyond doubt a fact that had already been often admitted without experimental foundation,

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[43] Landrieu, *Bull. soc. chim.* (4) **31**, 1217 (1922).

i.e., that when isomorphous substances associate to build up a mixed crystal, the lattice is a unique one and that the vicarious elements replace one another, atom for atom.

Thus Rinne[44] by comparing the photographs of minerals consisting of isomorphous mixtures of alkali halides and of carbonates of bivalent metals (aragonite series) with those of the parent salts was able to show that the lattices are rectangular in both cases, except for the necessary small changes in their unit distances. Still more conclusive is the work of Vegard[45] who investigated the systems: $KCl + KBr$ (cubic), $KCl + NH_4Cl$ (cubic), and $K_2SO_4 + (NH_4)_2SO_4$ (orthorhombic). The lines on the photographs of mixed crystals always occupy positions intermediate to those of the pure components, and nowhere do new lines appear. In the case of KCl and KBr, both of which belong to the same type, the length of the unit cube is a strictly additive function. The mixed crystals of $KCl + NH_4Cl$ belong to the type of the former. The sharpness of the lines proves that the isomorphous atoms or groups have the same diameter in mixed crystals. Thus NH_4 has a smaller diameter in the mixed crystal of the KCl type (face-centered cube) than in the crystals of the NH_4Cl type (body-centered cube). An extension of this type of experimental research is highly desirable and will not fail to bring very fruitful results.

The same substitution theory of solid solution is supported by Rosenhain[46] on the ground of X-ray work by Owen and Preston and by Bain in the paper already referred to. According to Bain, when a metal A acts as a solvent in taking up metal B in the solid state, the atoms of B replace atoms of A in the A space lattice. This substitution alters the parameter of the lattice slightly, but never its type until the limit of solid solubility is reached, at which point a new lattice is formed compatible with the increased atomic ratio. A very interesting fact discovered by him is that in cases where thermal analysis would indicate a continuous series of mixed crystals, as in Cu

[44] Rinne, *Centr. Mineral. Geol.* **1919,** 161.

[45] Vegard, *Z. Physik.* **5,** 17 (1921).

[46] Rosenhain, *Chem. Met. Eng.* **28,** 442 (1923).

– Mn and Fe – Mn, there is really a change of type; this is compatible with the absence of a gap in the composition of solid solutions, provided only that the solubility of A in solid B reaches the composition of saturated B and A. Still more interesting is the fact that, contrary to what would be expected, the composition ranges of the different types sometimes overlap, so that in this interval two solid solutions, may exist simultaneously. This was observed clearly in Fe – Mn alloys. Bain states that the alloys had been cooled very slowly and approached equilibrium at room temperature. A further proof that this coexistence is compatible with true equilibrium would nevertheless be very welcome. But there are a number of truly continuous solid solutions series exemplified by Cu – Au, Ag – Au, Cu – Ni, where the lattice changes insensibly from the one to the other pure constituent.

Rosenhain seeks to explain by very ingenious reasoning the principal change of properties of metals when they dissolve some other metal in solid state, e.g., their hardness, brilliance, melting range, etc., by the amount of local and general distortion caused in the space lattice by the stranger atoms.

I may be permitted to remind you that twenty-two years ago I ventured to say[47] that always when mixed crystals are formed, even to a limited extent, we have to do with a case of isodimorphism, a conclusion which was then largely criticized by crystallographers. I shall quote my statement: "In general one may take it as probable that when one crystal dissolves in another, the latter so to speak forces the solute to crystallize in the habit of the solvent." This proposition, which at that time sounded heterodox, would today be scarcely disputed. To put it in modern terms, and adopting the picturesque language of Rosenhain, we must admit that the "host" compels its "guests" to adapt themselves to its space lattice.

There are some cases of anomalous formation of solid solutions which it would be very interesting to study by the new methods, e.g., those formed by iodine with benzene[48] and with

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[47] Bruni, I, p. 31.

[48] Beckmann, *Z. physik, Chem.* **17**, 107 (1895).

cyclohexane. To see if this surprising formation of mixed crystals is connected in some manner with the constitution of the solvent, I tried the hexahydro derivative of benzene, cyclohexane, and found that iodine is capable of dissolving in solid state in hydrocarbons containing the hexatomic carbon ring without additions. It has in fact been found that with other aromatic hydrocarbons such as xylene, diphenyl and napthalene, no solid solution is formed.

We now come to another momentous question: how are the vicarious atoms distributed throughout the space lattice? Are they distributed irregularly or are regular groupings and configurations formed? Vegard in the paper just referred to concludes in favor of the first alternative, because a regularity in substitution would give rise to new lines; he thus says the substitution is totally random, and he defines mixed crystals as bodies characterized by unordered atomic substitutions. Contrary to this view stand the great bulk of observations made by Tammann and his pupils[49] of which it is possible to give here only a short sketch.

The technique of this work consists in testing the resistance of binary mixed crystals of different concentration to chemical or electrochemical actions capable of differentiating the two constitutents. The most studied were the metallic mixed crystals. For example, the Ag−Au and Cu−Au alloys were tested with no less than 20 different reagents, metallic salts, acids, oxidizers, sulfides, etc. Further, the electrochemical behavior was investigated through potential measurements. The chief result was the discovery of the "limits of resistance," i.e., the variations of the intensity of action with the concentration of the solid solution are not continuous but show certain limits which in cubic crystals can be expressed as multiples of

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[49] See particularly: Tammann, "Die chemische und galvanische Eigenschaften von Mischkrystalle und ihre Atomverteilung," *Z. anorg. allgem. Chem.* **107,** 1-233 (1919). Many papers in *Gottinger Nachrichten* 1916–1919. *Z. anorg. allgem. Chem.* **112,** 233; **114,** 281 (1920); **116,** 206 (1921); **118,** 48, 95 (1921). *Z. Elektrochem.* **28,** 36 (1922). Tammann and Vaders, *Z. anorg. allgem. Chem.* **121,** 193 (1922). Sauerwald, *Z. anorg. allgem. Chem.* **111,** 243 (1920). Creutzfeld, *Z. anorg. allgem. Chem.* **121,** 25 (1921).

1/8 mol of one of the two constituents. For example, silver-gold and copper-gold alloys containing more than 0.5 = 4/8 mol Au yield at 115° only minute traces of Ag or Cu to nitric acid, those with less than 0.375 = 3/8 mol Au give up practically all the less noble metal. Those comprised between 3/8 and 4/8 lose amounts inversely proportional to the Au content. In a series may be found several limits with different reagents. Thus in the Cu – Au series three resistance limits were found, namely, 1/8, 3/8, and 4/8, while only one electrochemical limit exists at 4/8 Au. The sensitivity of the several methods of attacking the alloys is very different and in some cases not very great. The sharpness in the fixing of the limits may vary considerably; sometimes they correspond to multiples of 1/8 mol within the limits of experimental errors, sometimes the multiples are surpassed or not wholly reached. The nature of the surface of the piece to be tested exerts a considerable influence on the situation of the action-limits. Polishing with a fine emery paper is sufficient to displace the limit to a higher Au content. The same displacement is effected by mechanical working, e.g., by cold rolling and heating. These treatments seem to increase the reactivity of the alloy. The conditions for the occurrence of limits are that the mixed crystals represent a real equilibrium and that the test be executed at a temperature at which a change of place between atoms is not possible. These conditions are thus found with mixed crystals obtained by solidification of molten alloys and annealed for a sufficient time; they disappear when by raising the temperature the diffusion becomes noticeable.

Mixed crystals obtained at low temperatures, e.g., by electrolysis of a mixed aqueous solution, have a totally irregular distribution and do not show any limits. This is not to be attributed to the electrolytic process in itself, since Sauerwald has found that Cu – Zn alloys, obtained through electrolyzing molten salts at 300°, are very near to complete equilibrium. In addition to metallic alloys Tammann endeavored to investigate from the same point of view non-metallic binary mixed crystals. The case presents here more difficulties, because isomorphous salts generally show similar reactions and solubilities. Nevertheless he found a suitable instance in the pair, NaCl+AgCl, which deposits from the molten mixtures a continuous series of mixed crystals. They were extracted with water, and it was found that crystals with less than 5/8 mol AgCl yield practically all their NaCl, while those with more than 6/8 mol lose none of it. Tammann further developed the notion of isomeric mixed crystals, i.e., mixed crystals which at the same composition have different properties, according to the condition under which they were produced. Mixed crystals of $NaNO_3+AgNO_3$ obtained from a mixed solution in alcohol-water yield more $AgNO_3$ to a saturated $NaNO_3$ solution than those deposited from a molten mixture and tempered. The same was found with AgCl+NaCl solid solution. But it may well be considered that this result could be due to the different natures of the surfaces of the two kinds of crystals owing to the conditions under which they were formed. An extension of such experiments would be highly desirable.

From these results Tammann draws his fundamental conclusion that the arrangement of vicarious atoms in mixed crystals, when equilibrium is reached, is regular. The limits are due to the protective action that the nobler atoms exert on the atoms of the less noble elements when they are in suitable numbers and positions. These conclusions are discussed by Masing[50] who deduces mathematically that the existence of action-limits does not require necessarily a regular distribution, but is compatible with a statistically irregular partition under certain simple hypotheses. It is further interesting to note that Bain was not able to discover by X-ray study any discontinuity in the Ag−Au and Cu−Au solid solutions series, corresponding to the limits found by Tammann in the same series.

APPLICABILITY OF THE LAWS OF SOLUTIONS TO SOLID SOLUTIONS

Are the laws of dilute solutions applicable to solid solutions as van't Hoff postulated in his fundamental paper? In order

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[50] Masing, *Z. anorg. allgem. Chem.* **118**, 293 (1920).

to solve this problem a preliminary question must be answered first: Does the chemical molecule continue to exist in the crystalline state?

Soon after the announcement of the first results of X-ray analyses there was a tendency to answer this question in the negative and to affirm that within the crystal edifice only atoms exist and the molecule vanishes into the lattice. But the reaction against this premature statement is now strong and the reasons for it have been very forcibly stated by Tutton.[51] Particularly decisive in this regard are the researches of Sir William Bragg[52] and of Shearer[53] the results of which may be thus summarized, that the chemical molecules enter into the crystals intact, and that the crystal units are composed of two or four, or other small number of chemical molecules. For example, the crystal unit of naphthalene is composed of two molecules, that of α-napthol and β-naphthol of four molecules. In simple cases, as rock salt, the division into molecules becomes very faint or apparently indistinguishable, but in the complex organic bodies it remains very clear. This preliminary question being thus disposed of we may proceed to the main problem.

It is well known that the confirmation of the van't Hoff theory is chiefly based upon the concordance of the values of the partition-coefficient between solid and liquid solutions directly ascertained with those deduced from the results of cryoscopic measurement, under the assumption that the molecular weight is equal in both phases.[54] The following equation was applied:

$$\alpha = \frac{\text{C solid}}{\text{C liquid}} = 1 - \frac{\Delta\,\text{Q}}{0.02\ \text{T}}$$

where Δ is the lowering of the freezing point of the solvent, Q its heat of fusion and T its (abs.) freezing point. Five quantitative determinations are available: iodine in benzene, thiophen

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[51] Tutton, *Ann. Reports* **18**, 210 (1921); **19**, 234 (1922). The same for 1922, London 1923. (Chapter on Crystallography.)

[52] Bragg, *J. Chem. Soc.*, **121**, 2766 (1922).

[53] Shearer, *Proc. Phys. Soc. London*, **35**, 81 (1923).

[54] See Bruni III, pp. 15–18, Bruni IV, pp. 61–68.

in benzene,[55] iodiform in bromoform, piperidine in benzene,[56] piperidine in cyclohexane[57] in all of which a good concordance was found, within the limits of error. A further confirmation came from the measurements of vapor pressure of organic solid solutions made by Speranski.[58]

From these results the conclusion had been drawn that the dissolved substance possesses the same molecular weight in solid as in liquid solution, i.e., it exists in the mixed crystals as single, or in some cases as double, chemical molecules. This conclusion can however hardly be maintained today in this simple form. If the crystal molecule of the solvent itself, like that of benzene, consists of four chemical molecules, it should be absurd to admit that those of the solid solute, thiophen or piperidine, be formed of only one. But the regularities found by Beckmann, Mascarelli and myself cannot be fortuitous. The two orders of facts can be easily reconciled on the basis that the partition-coefficient of a substance between two solutions is constant when the ratio between the molecular complexities of solvent and solute remains the same in both solutions. We thus arrive at the following very plausible conclusion: Thiophene has simple molecules in its liquid solutions in benzene and so has benzene in the liquid state; the crystal units of thiophene are double molecules like those of benzene and adapt themselves to the space lattice of the latter.

Other instances may be found. It is well known that naphthalene and β-naphthol furnish a continuous series of solid solutions which have been repeatedly studied.[59] Naphthalene has in pure liquid state, like other hydrocarbons, *simple* molecular weight; β-naphthol, like phenols and other hydroxyl derivatives, is associated in *double* molecules. From the solid solubility determinations of Küster, as well as from the vapor pressure of solid solutions according to Speranski, it was deduced

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[55] Beckman, *Z. physik. Chem.*, **17**, 120 (1895); **22**, 612 (1897).

[56] Bruni, *Gazz. chim. ital.*, **28**, I, 259, 277 (1898).

[57] Mascarelli, *Gazz. chim. ital.*, **40**, I, 31 (1910).

[58] Speranski, *Z. physik. Chem.*, **46**, 70 (1903); **51**, 45 (1905).

[59] Küster, *Z. physik. Chem.*, **17**, 357 (1895); **17**, 357 (1895). G. Bruni, *Gazz. chim. ital.*, **28**, II, 322 (1898). Speranski, *Z. physik. Chem.*, **46**, 70 (1903).

that β-naphthol in naphthalene solid solutions possesses also *double* molecular weight. Now we have seen that Sir W. Bragg has ascertained that the crystal-molecule of naphthalene consists of *two*, and that of β-naphthol of *four* chemical molecules. So we in fact see that the ratio is in both phases 1:2.

Interesting from this point of view are the colorations presented by some solid solutions, as indicative of the molecular state. As my observations seem to have passed unnoticed I shall recall them here. Organic substances containing the true nitroso-group linked to a C-atom are known to be intensely colored blue or green when they are monomolecular and to be colorless when bimolecular.[60] In liquid solutions and in molten state they are generally blue-green but sometimes colorless; pure crystals always colorless. Now Lobry de Bruyn and Jungius[61] observed that solid solutions of *o*-nitrosobenzoic acid in *o*-nitrobenzaldehyde obtained by exposing to light the crystals of the last named compound, are blue; but such solid solutions are always supersaturated and when their concentration surpasses a certain limit they decompose and the colorless crystals of the pure nitroso acid separate.

After that, together with Callegari,[62] I undertook experiments in nitrobenzene and *p*-nitrosotoluene dissolved in various solvents. The formation of solid solutions was tested by other methods and the color of solution, when liquid and after total solidification, was observed. The results are tabulated in the following lines and will prove sufficiently clear and convincing.

SOLUTE	SOLVENT	COLOR OF THE MIXTURE		
		Liquid	SOLID	
Nitrosobenzene.....	Benzene	Green blue	Colorless	No solid solution
	Nitrobenzene	Green blue	Green	Solid solution
p-Nitrosotoluene....	Nitrobenzene	Green	Colorless	No solid solution
	p-Nitrotoluene	Green	Green	Solid solution

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[60] See among others: Piloty, *Ber.*, **35,** 3090, 3093, 3101 (1902); Bamberger, *Ber.*, **33,** 3877 (1900); Alway and Gortner, *Am. Chem. J.*, 32, 400 (1904).

[61] de Bruyn and Jungius, *Rec. trav. chim.*, **22,** 298 (1903).

[62] Callegari, *Gazz. chim. ital.*, **34,** II, 246 (1906).

This result was then believed to imply that nitroso derivatives have a monomolecular structure in solid solution in the corresponding nitro-derivatives. This would now be corrected as stated above, namely that the ratio between the molecular complexity of corresponding nitro- and nitroso-derivatives is the same in liquid and in solid solutions.

An analogous result is found with iodine. Its liquid solutions in hydrocarbons or their hydrogenated derivatives have the pink-violet color characteristic of the diatomic molecule I_2. As above stated iodine gives solid solution with benzene and cyclohexane. These when totally frozen maintain, when sufficiently dilute, the same shade of color and no iodine crystals are separated, not even after many hours at −80°. But with solvents which are not capable of giving solid solutions, as bromoform and ethylene bromide, the violet color soon disappears to give place to the grey iodine crystals. In what manner this strange association really takes place is not easy to say; X-ray experiments would be welcome.

Objections were recently made by Tammann[63] to the validity of the solution law as extended to solid solutions. Owing to the authority from whom they originate I feel obliged to reply, although Tammann only repeats the arguments, formerly put forward by Küster,[64] which I have repeatedly refuted.[65] The objections are mainly based upon the fact that the partition coefficient between binary mixed crystals and the mixed solutions of both constituents in a liquid solvent does not remain constant, so that if the solution laws were applied, a continual change of molecular weight in the solid solutions would follow. Take for example a solubility isotherm of a pair of isomorphous salts A and B in water as represented by the diagram, figure 1. The isotherm does not generally conform to the diagnonal AB, but follows a curve like ACDB; this indicates that the partition coefficient changes, which according to Tammann should chal-

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[63] Tammann, *Z. anorg. allgem. Chem.*, **107**, 200–204 (1919).

[64] Küster and Würfel, *Z. physik. Chem.*, **50**, 65 (1904); Küster and Dahmer, *ibid.*, **51**, 22 (1905).

[65] Bruni II, p. 114–115; Bruni III, p. 18–20.

lenge the validity of the theory of solid solution. Now it is easy to see that the conclusion is by no means justified. The van't Hoff solution theory is a theory of dilute solutions and so should be that of solid solutions. It would not be reasonable to expect from the latter what nobody claims for the former. It is sufficient for the validity of the theory that the partition coefficient remain constant for dilute solid solutions, i.e., when one of the crystalline constituents may be considered as "solvent" and the other as "solute" or as Rosenhain says, "host" and "stranger." So it is sufficient that the end portions of the curve AC and BD can be considered as straight lines, which is really the case as it is shown from the diagram given by Tammann. Furthermore, the theory does not require the constancy of the

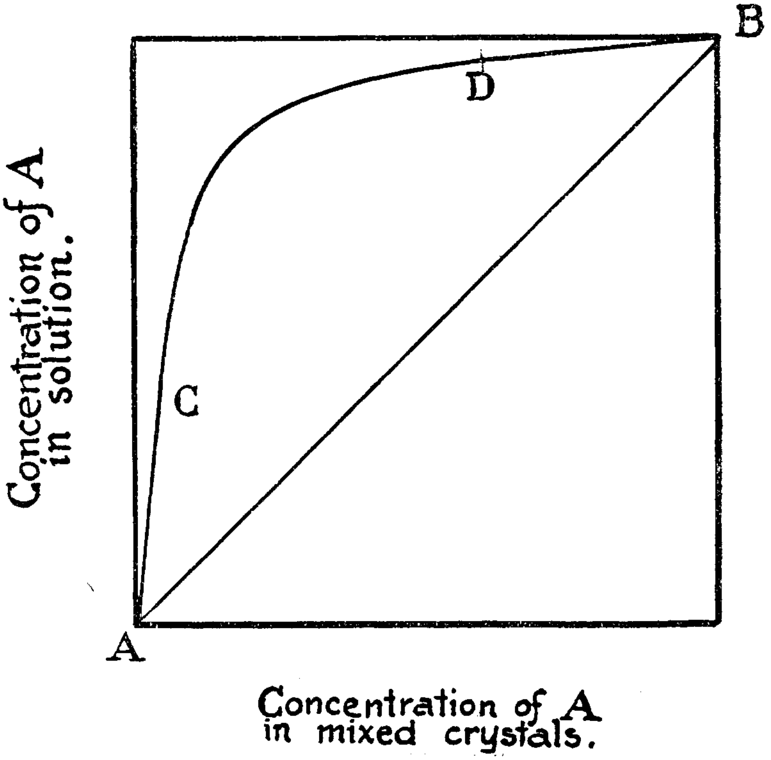

FIG. 1

ratio $\alpha = \frac{C_s}{C_e}$ but of the $\alpha = \frac{C_s^{1/n}}{C_c^{1/m}}$, where n and m is the molecular complexity of the substance in the solid (mixed crystal) and liquid solutions respectively. It was already said that for naphthalene and β-naphthol Küster found the coefficient $\alpha = \frac{C_s^{1/2}}{C_e} = 11.88$, which is in accordance with other facts. For the pair p-dichlorobenzene and p-dibromobenzene we have the experiments by Küster (cited above) and by Smits[66] on the partition between solid solutions and alcoholic solutions. Starting from the p-dibromobenzene corner the coefficient is practically constant; while from the other side there is a tendency to change.

Tammann further insists upon the fact that solid solutions of salts deposited from solutions never represent true equilibria, but I fail to understand how this can be an argument against the validity of the solid solution theory. It is true that this theory, as every other based upon thermodynamics, is only exactly applicable to systems which are in stable equilibrium, but this means only that in many cases of solid solutions where diffusion is very slow the application of the solution law is impossible. To deny the validity of the theory, it would be necessary to maintain and to prove that in these cases, e.g., at room temperature, diffusion does not exist at all and to divide the field of existence of mixed crystals into two ranges, within one of which diffusion occurs, while within the other it is impossible in principle. But this would hardly be possible. Küster[67] has actually proposed to distinguish solid solutions from mixed crystals on this basis, but Tammann himself[68] rightly observes that internal diffusion in all binary phases increases continually with the temperature, so that Küster's proposal is not rational. Summarizing the case I feel justified in stating that van't Hoff's theory, apart from its merits in stimulating research, maintains its full validity, provided of course that it be applied within the proper limits.

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[66] Smits, *Verslag Akad. Wetenschappen. Amsterdam*, **29**, 319 (1921).

[67] Küster, *Z. physik. Chem.*, **17**, 367 (1895).

[68] Tammann, *Z. anorg. allgem. Chem.*, **107**, 200 (1919).

SOLID SOLUTION AND CHEMICAL COMBINATION

The question of the relationship between mixed crystals and combinations, particularly addition compounds, is an old one. To give here a complete bibliography of the subject would be as tedious as unnecessary.[69] Among the older authorities I may cite Mallard[70] who was a partisan of the theory that between the two classes of substances there are transitions and that double salts are only a singular case of mixed crystals. The chief opponent of this doctrine was Retgers[71] who fought against it uncompromisingly; he maintained that the two classes are absolutely distinct and he felt justified in establishing the rule that mixed crystals and addition compounds exclude themselves reciprocally, trying with great ingenuity to prove that every conclusion against this rule is merely the result of faulty observations or of wrong interpretation. In the later period when the theory of solvates had been developed for the liquid solutions, particularly for those of the electrolytes, the opinion of Mallard found credit again. The discovery of the frequent formation of mixed crystals between intermetallic compounds and their components seemed to speak strongly for the existence of something intermediate between the two classes. But the question was really reversed, and instead of regarding double salts as mixed crystals with fixed proportions, the tendency was to consider the solid solutions as loose combinations, due to the action of homopolar affinities. This opinion was put forward by Abegg in the discussion following my lecture at the Congress of Rome.[72] In my Breslau[73] lecture I stated then the argument of both cases bearing on the existence of a transition between solid solutions and compounds.

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[69] For the old literature see: Arzruni "Physikalische Chemie der Krystalle," in Graham-Otto's Lehrb. d. Chemie, Vol. I, 3, p. 287-296.

[70] Mallard, *Bull. franc. soc. minéral.*, **4**, 100 (1881).

[71] Retgers, *Z. physik. Chem.*, many papers in Vols. **3-20** (1889-1897); see particularly, **16**, 577 (1895); **6**, 436 (1890).

[72] Abegg, *Sixth Intern. Congress App. Chem.* (Rome), **6**, Sect. X, 121 (1906).

[73] Bruni III, p. 22-25, 29-33.

Nernst[74] writes in the same sense, "The differences between physical mixture and chemical compound are differences of degree only, and between them all gradations occur." This view has recently been expounded by a distinguished crystallographer, Rinne,[75] who says that isomorphous mixtures behave "emphatically as transition members between chemical compound and physical mixture." Summarizing all the new evidence it now seems to me that the tide is turning again to the side of the Retger's theory.

The discovery of the action limits and of the regular distribution of atoms by Tammann might seem to lead us to consider mixed crystals as a sort of combination, but Tammann himself does not agree with this view, for he says unequivocally (*l.c.*, p. 186) that the assumption of chemical bonds between the two sorts of atoms would be quite superfluous and contradictory to the right interpretation of the action limits. He further (*l.c.*, p. 165) puts to himself the question how, from the atomistic point of view, a mixed crystal could be distinguished from a chemical compound having the same composition and the same space lattice. The problem arises particularly for mixed crystals exhibiting a constant melting point as corresponding to a maximum point of the liquid-solid curve, e.g., for Au – Zn. He answers in the following way; An eye which could discern the arrangement of the different atoms in the lattice would not be able to decide the question, but another more penetrating eye capable of seeing also the dispositions of the electrons around the several atoms would recognize the difference. For it would discern the rearrangements of the outer shells of electrons which take place in the act of a chemical combination, while the simple substitutions in the mixed crystals leave them unchanged.

A distinction between both these two views might be attempted on an energetic basis. Landrieu[76] states that a differentiation lies therein, that the heats of formation of mixed

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[74] Nernst, "*Theoretische Chemie*" (Berlin) 1900, 3rd Ed. p. 32.

[75] Rinne, "Die Kristalle als Vorbilder des feinbaulichen Wesens der Materie," (Berlin) 1921, p. 51–55.

[76] Landrieu, *Bull. soc. chim.* (4), **31**, 1217 (1922).

crystals are very near zero, while double salts are formed with appreciable development of heat. The first statement we have already seen does not correspond to the facts as solid solutions are generally endothermic. Thus the differentiation is still sharper than it was claimed to be by Landrieu. As for the addition compounds, he could have cited the work done by my friend Vanzetti[77] in my laboratory at Padua, on the heat of formation of organic addition compounds like *dl*-dimethyltartrate, *dl*-camphoroximes, and picrates of basic organic substances. In accordance with the difference in thermo-chemical behavior stands the well known fact that with increase of temperature the addition compounds easily dissociate, whereas the tendency to form solid solution is substantially increased. Very interesting from this point of view is the case of *d*- and *l*-camphoroximes which at room temperature form a true racemic combination, which changes by heating into a continuous series of pseudoracemic mixed crystals.

But the final decision must now come from lattice studies by the X-ray method. The most pregnant observations on this point are those by Rosenhain on intermetallic compounds. He remarks that if the latter be defined as homogeneous alloys in such a ratio as to conform to the law of multiple proportions it would be impossible to distinguish them from solid solutions, but as a matter of fact they have definite characteristics. For example, a definite X-ray spectrum has been found for the compound $CuAl_2$, which is very complex and quite different from either pure copper or aluminum. Doubtless in it, as in salts, copper and aluminum each builds up its own special lattice. This seems to be the distinguishing criterion between solid solutions and compounds. The former contains a single lattice where both kinds of atoms replace each other accompanied only by some distortion or change of unit dimensions. Compounds are constituted by the reciprocal interpenetration of at least two lattices.

Rosenhain further asks if intermetallic compounds can go into solid solutions as such and answers in the negative. He admits

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[77] Vanzetti, *Atti. accad. Lincei,* **22,** I, 103; **22,** 328, 379 (1912); **24,** II, 527 (1916).

that such a compound AB can dissolve partially one of its constituents, replacing its B atoms in their lattice by new A atoms or vice versa, but to go itself into solid solution the compound must dissociate. All this sounds very rational and plausible, but objections arise which still await explanation. Let us consider the case of the system Mg – Cd which exhibits the compounds MgCd giving a continuous series of solid solutions with both its constituents[78] or the analogous case Br – I where the solid solutions are interrupted by the compound BrI.[79] The existence of solid solutions over the whole range of concentration seems incompatible with Rosenhain's assumption. But it is possible that the series of mixed crystals are only apparently continuous and that there are three reciprocally overlapping series as found by Bain in the Fe – Mn system. According to Bain both magnesium and cadmium belong to the close-packed hexagonal type, but the parameters are considerably different, so that there will be a rather conspicuous distortion. The spectrum of the compound MgCd is still unknown. X-ray researches on this system are urgently needed.

When we proceed from metallic alloys to mixtures of salts things are more complicated. Let us take for instance the system $CaF_2 + CaCl_2$ studied by Plato.[80] They form mixed crystals in a limited range from both sides, and a double salt $CaF_2 \cdot CaCl_2$. We shall have on one side a Ca^+ lattice intermixed with a F^- lattice, with some F^- substituted by as many Cl^-, and on the opposite side the converse. In the middle we probably have a single Ca^+ lattice, a Cl^- lattice, and a F^- lattice regularly interpenetrated, in the Cl^- lattice some Cl^- may be substituted by F^-, or vice versa. But it would be futile to proceed further before more experimental data are at hand. There is here a big and promising program of research.

It would now be necessary to go on and consider the general question of isomorphism, that inexhaustible and fascinating

[78] Grube, *Z. anorg. Chem.*, **49**, 75 (1905); Urasow, *ibid*, **73**, 31 (1912); Bruni and Sandonnini, *ibid.*, **78**, 277 (1912).

[79] Terwogt, *Z. anorg. Chem.*, **47**, 203 (1905).

[80] Plato, *Z. physik. Chem.*, **58**, 350 (1907).

problem which for a century has attracted so many scientists from Mitscherlich to Langmuir. The theories of the latter author, and particularly his notion of isosterism, are the most promising contributions of the recent time and have already thrown much light on some points, and to revise the old material on its basis would be exceedingly interesting. But this must be reserved to a later paper, for this has already grown too long.

I cannot close without recalling an anecdote of twenty-two years ago, when I was working in van't Hoff's laboratory at Wilmersdorf, Berlin. Ostwald's campaign against atoms was then raging and atomism seemed indeed to be at its lowest ebb. One Sunday, during a colloquim, I had reported on some recent work on the differences of properties of crystals in the various directions. When I finished, van't Hoff took up the discussion and said: "Well, all this is very easy to understand. Let us take e.g. pyrrhotite, FeS, the Fe and S atoms will be disposed of in regular array in the edifice of the crystal. So you will have that on one face only Fe – atoms are present at the surface, and on another face only S – atoms, and on a third perhaps both kinds. So it is easily conceivable that chemical and physical properties will be different on the different directions and faces." We looked at each other and stood petrified, with all the admiration we had for him, we thought that this time the master had gone too far with his faith in atoms. But we were in the wrong and this was only another instance of the truly prophetic genius of the founder of the theory of solid solutions.