

On Eutexia

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the thick or the thin wire, as may be desired. In the instrument exhibited to the Society the stout wire is of german-silver 2.1 millim. in diameter, and of 0.2385 ohm resistance. The thin wire is of silver-platinum alloy; its diameter is 0.33 millim., and its resistance 8.21 ohms. The form of slider adopted is a much more well-conditioned arrangement than the usual heavy medal sliding key standing on three legs, and is more convenient in practice. The greater length of rheocord, though it renders the instrument less portable, increases the range of the instrument without affecting its sensitiveness.

XI. *On Eutexia.* By FREDERICK GUTHRIE*.

VII.

INTRODUCTION.—Although this memoir does not treat directly of the relationship between water and salts, the subject is so analogous with that examined in my memoirs on “Salt-Solutions and Attached Water,” that I have numbered the paragraphs in sequence with those of memoir VI. on that subject (Proc. Physical Society, vol. ii. p. 291).

The main argument of the present communication hinges upon the existence of compound bodies, whose chief characteristic is the lowness of their temperatures of fusion. This property of the bodies may be called Eutexia †, the bodies possessing it eutectic bodies or eutectics (εὐ τήκειν). It is at once apparent that the cryohydrates are essentially eutectic. It will, however, perhaps be better to make the term more useful by limiting its application. I shall use it, and I should like it to be used by others, for bodies made up of two or more constituents, which constituents are in such proportion to one another as to give to the resultant compound body a minimum temperature of liquefaction—that is, a lower temperature of liquefaction than that given by any other proportion. Here, again, the cryohydrates completely satisfy the definition. But it will be shown that they constitute only one term of

* Read May 24, 1884.

† Used in very much this sense by Aristotle. I should have preferred the word hypolytic; but I am instructed that, although sanctioned by its use in Chemistry, this employment of *ὑπό* is not strictly admissible.

a series ; that their melting or liquefaction is quite continuous with the so-called fusion of mixed metals or salts ; and that the eutectic alloys of metals, many of which have been long imperfectly known, and the eutectic alloys of salts, which I shall describe (§§ 207–229), are the perfect homologues of the cryohydrates. Let me, in a word, invite my readers, while looking upon water as fused ice, to trace the analogy between the behaviour towards solids of water on the one hand, and some other fused substance on the other.

Eutectic Metallic Alloys.

§ 195. Metals mix with one another in various proportions forming Alloys, many of which are in extensive use in the arts. Amongst the most instructive aspects of alloys is certainly that which results from a comparison of the properties of the alloy with those of its constituents. And, further to specialize, the discussion of the relation between the temperature of fusion of the mixed metal and the temperatures of fusion of its elements forms a chapter of the highest significance.

§ 196. In studying this chapter, I employ Bismuth as one of the elements on account of its low melting-point, and because it can be got very pure. Fused bismuth will be the homologue of the water or fused ice of my previous memoirs, and the metal with which it forms alloys will be the homologue of the salt. The bismuth used in the following experiments melted at 263° C.

§ 197. *Bismuth and Zinc.*—It has been asserted that when bismuth and zinc are melted together two alloys are formed which do not mix, the upper being an alloy of 2·4 bismuth and 97·6 zinc, and the lower of from 8·6 to 14·3 bismuth and from 91·4 to 85·7 zinc (see § 206). Such a condition and such a ratio may accidentally exist ; but is only occasional. Let bismuth be fused and heated to about 350°, and let as much melted zinc be added in small quantities at a time as the bismuth will form a liquid alloy with at about that temperature. Let now the temperature be watched until it has sunk to about 250°. The liquid is run off and a little bismuth is added to the contents of the crucible, which is heated until fusion ensues, and a second amount of liquid at 250° is again obtained. This and the quantity obtained by the first process

are melted together and allowed to cool gradually. The temperature sinks almost immediately to 248° , and remains constant at that temperature. The alloy maintains the same temperature to the very last, and is the eutectic alloy of these metals. It showed on analysis :—

	Per cent.	Melting temperature.
Bi	92·85	} 248° .
Zn	7·15	

Of course this eutectic alloy is now to be made by melting the metals together in the above ratio ; but on account of the oxidation of the zinc at about its melting-point, it is better to provide a little excess of that metal and to remove the excess by the above method.

§ 198. *Bismuth and Tin*.—In forming the eutectic alloy of these, the bismuth need be only just fused. A roll of tin foil is stirred into the bismuth, and in spite of the cooling effect, the alloy which is formed remains liquid. When the temperature reaches about 150° , the roll of tin is withdrawn, and the temperature is watched as the alloy cools. The temperature ceases to fall at 133° , which is the fusion temperature of this eutectic alloy. Having satisfied oneself of this, the whole may be remelted, and about a quarter having been allowed to solidify at 133° , the rest is poured off, and is pure. This alloy is very finely crystalline when quickly cooled; it is very brittle and its freshly broken surface closely resembles that of cast iron. It showed on analysis :—

	Per cent.	Temperature of fusion.
Bismuth	46·1	} 133° .
Tin	53·9	

§ 199. *Bismuth and Lead*.—Proceeding in a very similar manner as with tin, a fixed temperature of $122^{\circ}\cdot7$ is reached. This eutectic alloy has the composition :—

	Per cent.	Temperature of fusion.
Bismuth	55·58	} $122^{\circ}\cdot7$.
• Lead	44·42	

It is of a bluish grey, is malleable and easily cut or sawn.

§ 200. *Bismuth and Cadmium*.—On adding melted cadmium to melted bismuth and proceeding as above, it is possible to obtain an alloy whose melting-point is 144° C. It shows, on analysis, the following composition :—

	Per cent.	Temperature of fusion.
Bismuth	59·19	} 144°.
Cadmium	40·81	

§ 201. So that we have the following results :—
Eutectic alloy of Bismuth with

	Per cent.		
Lead	contains 44·42 lead	and melts at	122·7°
Tin	,, 53·90 tin	,,	133
Cadmium	,, 40·81 cadmium	,,	144
Zinc	,, 7·15 zinc	,,	248

These weight-ratios are none of them simple atomic weight-ratios. Of course, in many cases, metals can be fused together in simple multiples of their atomic weights, but in most such cases, on cooling the alloy, one of the metals will separate out first and so destroy the ratio. In other cases an alloy richer than the original alloy in regard to one of the metals, and therefore a homologue of a suberyohydrate, separates, and the original ratio is again disturbed. When we are dealing with metals which, like antimony or arsenic, on the one hand, are themselves halogenous, or with such strongly chemico-positive metals as sodium on the other, we may and do get alloys of atomic composition—metallo-metallic salts. But the temperatures of fusion of these are never, as far as I am aware, lower than that of either (both) of the constituents. They are not eutectic. Nor is it easy to see any reason whatever why they should be so. On the contrary, we should expect such an alloy to be soluble in one or other of its elements, with depression of temperature. The statement therefore that alloys of minimum melting-points are got on mixing the metals in certain simple ratios of their atomic weights, is presumably to be put on one side. As the cryohydrate forms itself when a salt-solution of any strength loses heat, so the eutectic alloy forms itself when an alloy whose constituents are in any ratio is cooled. The only exception to this is when the constituents

are in the ratio homologous with that between the constituents of the suberyohydrate. So-called "fusible alloys," or "fusible metals," are imperfect eutectic alloys. And it is seen that the melting-points obtained by previous experimenters with bismuth-tin and bismuth-lead are considerably higher than those above shown (see also § 206).

§ 202. Further, if we take the eutectic alloy of bismuth-tin and that of bismuth-lead, and treat them together as though they were single metals, we get the eutectic alloy of the three metals; or either of these alloys with bismuth-cadmium gives a corresponding tri-eutectic.

These and certain other tri-eutectic alloys may form the substance of a further communication. They stand in the closest connexion with the cryohydrates of mixed salts, which were discussed in §§ 109–116.

§ 203. Again, a tetra-eutectic is obtained either by building up from the tri-eutectic and a metal, or from three eutectics; or perhaps more readily, although with greater waste of metal in the first tentative experiment, by fusing the four metals together. The three eutectic bismuth alloys above described were fused together in considerable quantity and in indefinite ratio. As the mass had only partly solidified at 100°, it was pressed in a linen bag under boiling water. The liquid portion was further cooled. A large amount remained liquid at 71° C.; at which temperature the thermometer thenceforth stood until the whole was solid. On remelting several times, and collecting that which remained liquid after about a fifth had solidified, the eutectic alloy of bismuth-tin-lead-cadmium was obtained pure. It showed the following composition:—

Bismuth	47·45	47·38
Lead	19·39	19·36
Cadmium	13·31	13·29
Tin	20·00	19·97
	100·15	100·00

The question, very interesting to mineralogists, immediately arises, Can a tetra-eutectic alloy be made without loss by mixing three dieutectic alloys in some proportion with one another? The answer is in this case certainly in the negative.

For according to § 199, 19·36 of lead require 24·25 of bismuth. Again, according to § 200, 13·29 of cadmium require 19·27 of bismuth, and according to § 198, 19·97 of tin require 17·08 of bismuth. So that to satisfy the three metals lead, cadmium, and tin eutectically, 60·52 of bismuth would be required, instead of 47·45.

The above alloy is extremely closely grained and brittle. It may, however, be bruised and rolled. It takes a high polish. When in some thickness its fracture is conchoidal, exposing steel-grey surfaces. This highly eutectic alloy may find uses in the arts, as with the exception of alloys containing mercury and those of potassium and sodium, it has a melting-point lower than any alloy before described.

§ 204. The above experiments, in which bismuth replaced the ice of my previous experiments with salt-solutions and some other metal replaced the salt, are of course only a few of an innumerable series of series. But they will serve to show the genesis of bodies of this class. I have already* pointed out how the "de-leading" of the lead-silver alloy in Pattinson's process is really analogous to the separation of ice from a salt-solution. The residual liquid alloy should have a composition analogous to that of a cryohydrate, and should be the eutectic alloy of lead-silver. If this be so, its temperature of fusion should be lower than that of lead itself; and that it is so is proved by the separation of solid lead from the melted mass. It is well known that Pattinson's process may be "pushed too far." According to the above interpretation, this simply means that when the fusion-temperature of the eutectic alloy is reached, this body solidifies as a whole and is raked away as the lead had been. A pyrometer, an air thermometer, in the mass would be an absolutely trustworthy guide as to the proper time for cupellation to replace "de-leading."

§ 205. That certain metals may and do unite with one another in the small multiples of their combining weights may be conceded. To such bodies the eutectic alloys bear the same relationship as the cryohydrates bear to the common hydrates, and, like the latter bodies, their constituents are not in the ratio of any simple multiples of their chemical equiva-

* R. Inst. Lecture, Feb. 16, 1877.

lents. But their composition is not, on that account, the less fixed, nor are their properties the less definite. Many of these eutectic alloys have been known in partial purity for ages, having been nearly reached by repeated trial or by assuming a molecular ratio. But they have not been recognized as a class numbering merely as diectectics several hundred (say 1700), which can be obtained, as above shown, systematically and in a state of great purity. Nor does the fact that several instances are known in which metals combine with one another in the chemical sense—that is, in simple multiple ratio by weight of their combining weights and with liberation of heat—at all diminish the possible number of such eutectic alloys. For, firstly, as a salt may unite with water, as when anhydrous chloride of calcium does so, to fix the water as crystalline water, and also may unite with water as a cryohydrate, so two metals may unite in one proportion while they form a definite eutectic alloy in another. Secondly, the very bodies resulting from the chemical union of the two metals will possibly, and probably, furnish starting-points of new series of eutectic alloys, consisting of a single metal on the one hand and the chemical alloy on the other.

§ 206. It will be instructive to compare the results given above with results obtained by some previous experimenters who have examined bismuth alloys.

According to Rose, one part by weight of lead, one of tin, and two of bismuth melt at $93^{\circ}75$. That a part of it may melt, and so the whole soften at that temperature, need not be questioned. But that the whole should melt from first to last at any fixed temperature, is so highly improbable as to be practically impossible on account of the simplicity of the proportion.

According to Matthiessen and v. Bose zinc and bismuth form two alloys, one containing 97.6 of zinc, and the other from 8.6 to 14.3 (instead of 7.15), which two alloys are immiscible. The melting-points do not appear to have been given. Indeed, as neither of these is eutectic, so neither has a proper melting-point.

The nearest approach to an eutectic alloy appears to have been made by Rudberg, who, on melting together 177 parts by weight of tin, and 213 of bismuth (tin = 45.38 per cent., bismuth = 54.62 per cent.), obtained an alloy which is said

to have a constant melting-temperature of 143° . Rudberg further states that all other ratios have higher melting-points, and that, on cooling, the liquid portion reduces itself to this ratio. The above ratio is intended for that between three "atoms" of tin and two of bismuth. For if the atomic weight of tin be 118 and that of bismuth 210 (Rudberg takes tin 56, bismuth 106.5), we should have in Sn_3Bi_2 the percentage, tin = 45.74 per cent., bismuth = 54.26 per cent. It has been shown above that the true eutectic alloy has a melting-point 10° lower than Rudberg's, and the composition, tin = 53.9, bismuth = 46.1 per cent.

Again, it is stated that when lead and bismuth are fused together, in the proportion of three atoms of lead to two of bismuth, an alloy is obtained whose melting-point is constant at 129° . This ratio requires lead 42.49, bismuth 57.51 per cent. The true eutectic alloy has a melting-point $6^{\circ}3$ C. lower, and, as we have seen, has the composition, lead 44.42, bismuth 55.58.

The preconceived notion that the alloy of minimum temperature of fusion must have its constituents in simple atomic proportion,—that it must be a chemical compound,—seems to have misled previous investigators. Such misconception could scarcely have arisen if the existence and properties of the cryohydrates had been known.

§ 206 A. It was shown many years ago (about 35) by my brother Francis, that if two counties are only then supposed to be in contact when they have linear common boundary, to colour a map so that no two counties in contact shall be coloured alike, four colours at most are needed. Taking the special case in three dimensions it is clear that five, but no more spheres, may touch one another (each touching all). If there be such things as atoms, and if they be spherical or of one curvature, not more than five can touch, each touching all. Chemical compounds are known containing more than five elements. But this circumstance does not obliterate the limit of the eutexia of alloys, which are neither atomic nor molecular.

Salt Alloys.

§ 207. It cannot be gainsaid that, vast as is the importance in the arts of the elementary metals and their alloys, yet in

terrestrial nature the interaction and relationship of compound bodies is at least of equal importance, and of far wider scope; for the science of such interaction and relationship constitutes the greater part of chemistry and petrology.

Amongst the non-metallic elements we should expect the class analogous with the eutectic alloys to be very restricted in number, on account of the chemical attitude of such elements towards one another, that is their tendency towards chemical union.

Chemical compounds, however, all of which may for brevity's sake be called salts, can give rise to an indefinite number of eutectic bodies; indeed to an indefinite number of series of such bodies. The whole of the preceding memoirs on Salt-solutions and Attached Water are in fact mainly a study of one such series. The cryohydrates are nothing else than eutectic alloys of the one salt called water with the various other salts. If instead of fused ice (water) we employ another fused salt, say fused table salt, we may expect to find it forming eutectic alloys with other salts, whose characteristic should be fusibility at a temperature lower than that of either (both) of its constituents.

§ 208. In choosing salts whose behaviour under such examination shall be as free as possible from ambiguity we must avoid:—

First, those which are decomposed when heated by themselves to anything like the temperature to which they are to be exposed in the experiment. And we are safe in this respect, if we confine ourselves to those which are not decomposed on fusion. For the bodies we are seeking should have temperatures of fusion below the temperature at which that one of its constituents fuses whose temperature of fusion is the lower of the two—it should be eutectic.

Secondly, must be avoided those which react on one another chemically, either in the sense of suffering double decomposition, or in that of direct combination whereby double salts are formed. It will be shown in § 225–227 that it is not always necessary to avoid the first of these contingencies. The possibility of double decomposition is of course avoided when the two salts used have either a common basic, or a common acid constituent.

Thirdly, are to be eschewed those salts which attack at high temperatures the vessels employed.

Amongst all salts perhaps Nitre answers these requirements best, as the body whose homologue is ice in the previous memoirs of Salt-solutions and Attached Water Nitrates do not form double salts with one another, nor with other salts (compare, however, Karsten). Nitre may be raised without suffering decomposition to a temperature far above its temperature of fusion; possessing in this respect a wider range of available temperature than nitrate of ammonium, which might otherwise be preferable on account of its lower melting-point.

§ 209. In the following paragraphs, from § 210 to § 227, temperatures up to 280° C. were measured by means of a mercurial thermometer. Those above that range were determined by an air-thermometer with a horizontal stem about three feet long. The index was a plug of mercury. The total range was from about 0° to 380° C. As most of the experiments in which the air-thermometer was used were made on days on which the barometric pressure was nearly the same, no correction was needed. On other days the air-thermometer was standardized at the temperature of boiling water, with the mercurial one placed by its side in the water.

§ 210. *Nitre*.—I find that the temperature of fusion of pure nitre is 320° C.

§ 211. *Nitre and Chromate of Potassium*.—If nitre be fused in a large porcelain crucible and neutral chromate of potassium be added, some of the chromate is dissolved. The higher the temperature the larger the quantity. On suffering the solution to cool slowly, chromate of potassium separates out in fine powder, which sinks through the fused mass. The temperature falls till it reaches 295° , at which it remains constant; and the liquid begins to solidify. The liquid portion is poured into a fresh crucible; and this may be repeated any number of times. The temperature of solidification is constant. The liquid being poured upon a cold slab solidifies to a mass, which has when cold precisely the colour of sulphur. Of this alloy 2.4881 grams gave 0.1226 chromate of barium. This corresponds to 0.0936 chromate of potassium, which is 3.76 per cent. Accordingly this alloy is:—

		Melting-point.
Nitre	96·24	}
Chromate of potassium	3·76	
		295°.

§ 212. *Nitre and Nitrate of Calcium.*—The three metals calcium, strontium, and barium promised to be of interest in furnishing nitrates alloyable with nitre. The method of experiment was precisely as before, the nitrates having been rendered anhydrous before they were added to the fused nitre. The bases were all separated and weighed as carbonates.

The eutectic alloy of nitre with nitrate of calcium has a melting-point of 251°. Of this, 1·8300 gram gave 0·2830 carbonate, or 0·4641 gram nitrate of calcium. This corresponds to 25·36 per cent.

§ 213. The eutectic alloy of nitre with nitrate of strontium has a melting-point of 258°. Of this, 1·9490 gram gave 0·3498 gram carbonate, or 0·5031 gram nitrate. This corresponds to 25·81 per cent.

§ 214. The eutectic alloy of nitre with nitrate of barium melts at 278°·5. Of this, 2·6100 grams gave 0·5860 gram carbonate, or 0·7773 gram nitrate of barium. This corresponds with 29·53 per cent.

Eutectic alloys of :—

		Melting-point.
Nitre	74·64	}
Nitrate of calcium	25·36	
Nitre	74·19	}
Nitrate of strontium	25·81	
Nitre	70·47	}
Nitrate of barium	29·53	
		278°

In this group strontium holds its accustomed intermediate place between calcium and barium; but, both in regard to the melting-point and to the composition of its eutectic alloy, it more closely resembles the former than the latter.

§ 215. *Nitre and Nitrate of Lead.*—The eutectic alloy formed by these salts is of great interest, not only because the lead element, like the chromate of potassium and the nitrates of barium and strontium, cannot be fused alone without decomposition, but because it, the alloy, has a remarkably low melting-point, and because either constituent in excess of its quantity in the eutectic alloy raises the melting-point in a manner easy

to be followed. To the fused nitre the dry nitrate of lead is added, and on cooling one or other separates out in crystals easy to distinguish. More of the salt which is in fusion is added, until this is in its turn the one which separates on cooling. The same process having been repeated three or four times, the whole is allowed to lose heat as before. The temperature soon settles at 207° C., and thereupon the liquid begins to solidify as a beautiful white opaque porcelain-like mass, startlingly like the cryohydrates. The temperature may at first sink to 203° C.; and when in this condition of supersaturation, solidification is not to be induced by the introduction of dust of either of the nitrates, but begins when dust of the solid eutectic alloy is introduced. The temperature thereupon rises to 107°. This presumably proves that the alloy has a crystalline form of its own, different from those of its two constituents. Its composition was as follows, the lead being weighed as sulphate. The two specimens were from separate preparations, the only criterion of identity of composition being identity of melting-point.

(1) 2·8625 grams gave 1·2150 of sulphate of lead, or 1·3276 gram of nitrate of lead, or 46·38 per cent. of nitrate of lead.

(2) 2·3005 grams gave 0·9968 gram of sulphate of lead, or 1·0892 gram of nitrate of lead, or 47·34 per cent. Taking the mean, we have

Eutectic alloy of

	Melting-point.
Nitre	53·14
Nitrate of lead	46·86
	} 207°.

§ 216. *Nitre and Sulphate of Potassium.*— Anhydrous neutral sulphate of potassium dissolves in fused nitre, and separates out therefrom as the fused mass cools in the form of a fine powder. It is advantageous to allow the mass to lose heat very slowly. As soon as the porcelain-like eutectic alloy begins to be formed, the liquid is transferred into a fresh crucible, and the solidification is continued. An alloy is thus finally obtained of the constant melting-point of 300°.

2·6625 grams gave 0·0836 gram sulphate of barium, corresponding to 0·0627 gram sulphate of potassium, or 2·36 per cent.

Eutectic alloy of	Melting-point.
Nitre	97·64
Sulphate of potassium	2·36
	} 300°.

§ 217. Putting together the results of §§ 211–214, we have the following table, in which the alloys are, like the cryohydrates of table § 88, arranged according to the lowness of the melting-points.

TABLE XLIII.

Eutectic alloys with nitre.

Name of salt.	Temperature of fusion.	Per cent. of salt.	Per cent. of nitre.
Nitrate of lead	207°	46·86	53·14
Nitrate of calcium.....	251	25·36	74·64
Nitrate of strontium.....	258	25·81	74·19
Nitrate of barium.....	278	29·53	70·47
Chromate of potassium ...	295	3·76	96·24
Sulphate of potassium.....	300	2·36	97·64

Fused mixtures of nitre and the variable salt, which are richer in the salt than the eutectic alloy, give up that salt on losing heat; those which are poorer give up nitre, until in both cases the eutectic alloy is reached. The eutectic alloy is the exact analogue of the cryohydrate; and just as in the preceding memoir curves were drawn showing, on the one hand, the temperatures at which ice separates from salt-solutions of various strengths, weaker in salt than the cryohydrate, and, on the other, the temperature at which the salt, or occasionally a suberyohydrate, separates from such solutions as are stronger in salt than the cryohydrates, so, doubtless, the analogous curves could be drawn connecting the temperature at which solidification begins with the fused mixtures of salts (see § 223). And, again, as there are always two strengths of an aqueous solution, one stronger and the other weaker than the cryohydrate, which are both saturated at the same temperature below zero, one in respect to the salt and the other in respect to the ice, so with these fused mixtures there must be two such mixtures, from both of which a solid begins to separate at any given temperature between the melting-point of the most easily fused constituent and that of the eutectic alloy. § 223 is devoted to the tracing of this inquiry.

§ 218. The analogy is so perfect between the two groups of bodies (eutectic alloys and cryohydrates), that we may look with great confidence for homologous phenomena. The freezing mixture, or cryogen of my former memoirs, has its perfect counterpart amongst the salt-alloys, as follows :—

A layer of powdered nitrate of lead (46 parts by weight) is placed in the bottom of a wide test-tube. On this is laid a thin disk of mica, having a hole in the middle. A thermometer is fixed through the hole so that its bulb is half covered by the lead salt. Upon the mica, and so surrounding the top of the bulb, is piled some powdered nitre (54 parts). This tube is plunged into a bath of melted nitre, which is heated some few degrees above its melting-point, and until the thermometer registers about 250° . The thermometer is then used as a stirring-rod to mix the two salts. The mercury sinks to 207° , and remains pretty constant for a time at that temperature. The contents of the tube liquefy, and solid nitre is formed upon the outside of the tube. Now substitute ice for nitre, and perform the analogous experiment. The nitrate of lead and ice in the inner tube will form a freezing-mixture when stirred together, and this will cause ice to form on the outside, if the melted ice (water) in contact with it be not too warm.

§ 218A. Just as the eutectic metallic alloys had been nearly approached by Rudberg and others, so approximations to eutectic salt alloys have not been unknown. Thus M. Maumené (*Comptes Rendus*, 1883, xeviii. p. 1215) makes the very interesting statement that while neither nitrate of barium nor nitrate of lead can be fused *per se* without decomposition, they can both be so fused beneath a mass of nitrate of potassium or nitrate of sodium or a mixture of both. He states that an equivalent mixture of the nitrates of barium and sodium melts at about 370° ; and that when equal weights are taken, crystallization begins at 322° , and solidification takes place at 288° . Again, according to M. Maumené, equal weights of the nitrates of lead and sodium have a melting-point (*point fixe*) at 282° [we have seen that the eutectic alloy of these two fuses at 268° and contains 42.84 *per cent.* of nitrate of lead (see § 221)]. And again, M. Maumené, on taking equal weights of nitrate of sodium, nitrate of potas-

sium, and nitrate of lead, finds the melting-point 259° . [I find (§ 215) an eutectic alloy melting at 186° and containing 43·34 nitrate of lead.] It appears that none of the proportions given by M. Maumené are those of the eutectic alloys, and that accordingly the temperatures of solidification which he gives cannot be constant.

§ 219. *Eutectic Salt Alloys of Nitrate of Sodium.*—Nitrate of sodium fuses at 305° , and we might perhaps expect that its eutectic alloys would have lower fusing-points than the corresponding nitre alloys. The following experiments show that this is by no means the case.

§ 220. *Nitrate of Sodium with Nitre.*—Obtained by the method above described, the eutectic alloy of these two salts has the fusing-point of 215° C. Of this alloy 3·8885 grams were converted into neutral sulphates, having the joint weight 3·3135. This implies 2·5093 grams nitre and 1·3792 gram nitrate of sodium ; or

	Per cent.	Melting-point.
Nitrate of sodium . . .	32·90	} 215° .
Nitrate of potassium . . .	67·10	

For the specific gravity of this alloy, see § 228.

§ 221. *Nitrate of Sodium with Nitrate of Lead.*—This eutectic salt alloy has a melting-point of 268° . A weight of 3·3040 grams gave 1·2955 grams sulphate of lead, which corresponds to 1·4156 gram nitrate of lead.

	Per cent.	Melting-point.
Nitrate of sodium . . .	57·16	} 268° .
Nitrate of lead . . .	42·84	

§ 222. *A Tri-eutectic Alloy.*—Let us consider for a moment the alloy in § 219 to be a single salt, and find the eutectic alloy between this and nitrate of lead. The lowest melting-point is found to be 186° ; and the composition of the alloy, derived from the result that 2·9280 grams gave 1·1613 gram sulphate of lead or 1·2690 gram nitrate of lead, is as follows :—

	Per cent.	Melting-point.
{ Nitrate of potassium . . .	38·02	} 186° .
{ Nitrate of sodium . . .	18·64	
{ Nitrate of lead . . .	43·34	

This of course implies that the above is the eutectic alloy of

these three salts. The eutexia of salt alloys of more than two salts is a very wide question upon which I can only here touch.

§ 223. The following experiment completes the analogy pointed out in § 218. Mixtures of nitre and nitrate of lead, both in the form of powder, were made in different ratios from 95 nitre and 5 of nitrate of lead, 90 of nitre and 10 of nitrate of lead, and so on; these were put into test-tubes and heated in an oil-bath, which was kept continually stirred. The mixture was completely melted, and the temperature at which solidification began was observed. The observations, being repeated many times, gave the following results:—

Temperatures at which solidification begins in melted alloys of nitre with nitrate of lead of various strengths.

TABLE XLIV.

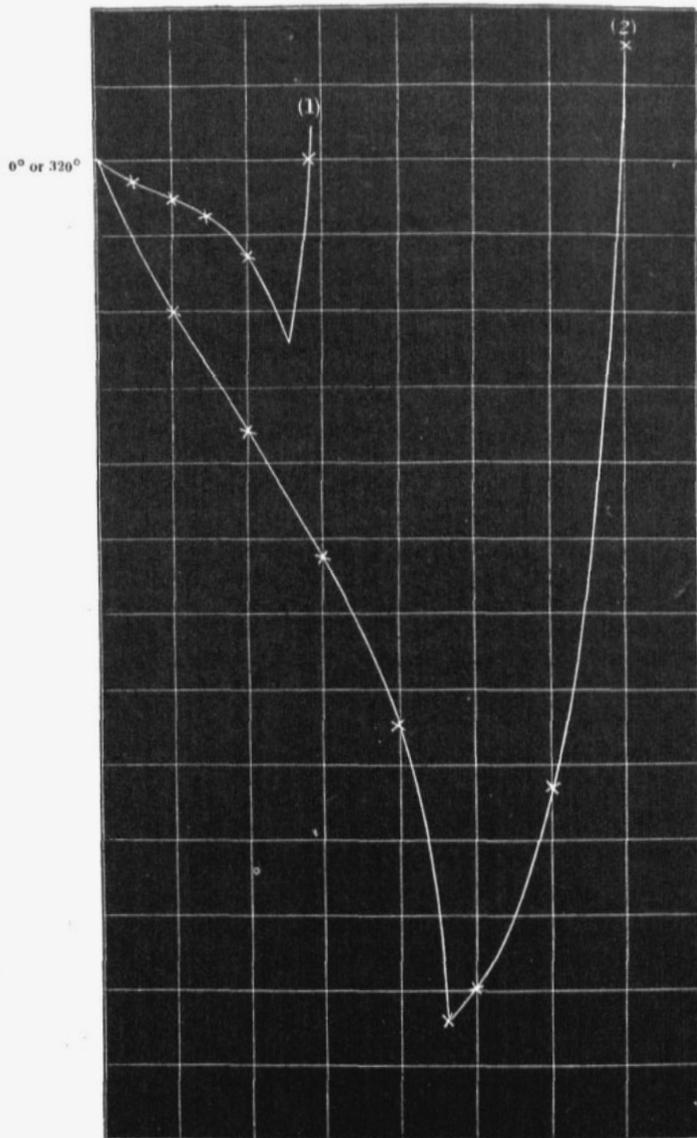
Nitre per cent.	Nitrate of lead per cent.	Temperature of beginning of solidification.	Nature of body separating.
100	0	320°	Nitre.
90	10	300	"
80	20	285	"
70	30	268	"
60	40	246	"
53.14	46.86	207	Eutectic alloy.
50	50	210	Nitrate of lead.
40	60	238	"
30	70	335 (?)	"

It is of course necessary to heat the mixed powders, in each case, beyond the temperature which proves to be the initial solidifying point of the mixed mass. On heating the column of powder it is noticed first to shrink and cake together to about a quarter of its former volume, reminding one of the baking of clays. Indeed all phenomena of so-called incipient fusion of compound bodies (the pasty state) may be due to what takes place here, namely the formation of an eutectic alloy.

The decomposition of both terms of this alloy, at temperatures not very much higher than 320°, puts a limit to the tracing of this curve further, but its general aspect is quite like that of the salt-solution (water) curves below zero, of which so many examples have been given in previous memoirs.

Mixtures consisting of 20 per cent. nitre and 80 per cent.

nitrate of lead, and even 10 per cent. nitre and 90 per cent. nitrate of lead, fuse together into clear liquids without decom-



position, but I have not determined the melting-points. At a higher temperature the red peroxide of nitrogen is evolved,

but I do not know whether it is or is not accompanied by oxygen.

In the figure curve (1) shows the solidification-temperatures of mixtures of nitrate of lead and fused ice (§ 152), and curve (2) shows the solidification-temperatures of mixtures of nitrate of lead and fused nitre. The abscissæ are on the same scale (1 millim. to 1 per cent. of lead salt). The ordinates are in (2) 1 millim. to 1° C. ; in curve (1) 1 millim. to 0° .1. The curve (2) is fetched down so that the two have a common origin.

§ 224. One of the widest generalizations with regard to the behaviour of compound bodies towards one another is that which assumes, in the case of two salts, that the bases are shared in the first place by the acids, and that the result which often ensues, that one base and one acid are ultimately found in union to the exclusion of all others, is due to the successive withdrawal of such a combination when formed, either by its insolubility or volatility. Accordingly we must not be surprised that when the conditions of insolubility are varied, the final selection may be wholly changed. The salt alloy described in § 215, namely the eutectic alloy of nitre and nitrate of lead, when mixed with the eutectic alloy of nitre and sulphate of potash, § 216, and heated, forms a perfectly transparent liquid. Sulphate of lead, which is so insoluble in water, is soluble in fused nitre (see § 225); and a mixture may be got identical with that got on heating nitrate of lead with sulphate of potassium in the presence of nitrate of potassium. There is in both cases equilibrium between the bases and acids. When sulphate of lead is dissolved in fused nitre, it is to be noticed that, at a considerably increased temperature, the red oxide of nitrogen is given off, as when nitrate of lead is heated by itself. Both nitre and sulphate of lead, when heated by themselves, require a much higher temperature for their decomposition; this seems to show the existence of nitrate of lead in the fused mixture. The liquidness of the fused alloy does not show that no sulphate of lead is present: a certain amount of lead is no doubt in union with sulphuric acid, but is soluble in nitre as other salts are soluble in water.

§ 225. *Nitre and Sulphate of Lead.*—On adding pure dry sulphate of lead to fused nitre, solution ensues the more

abundantly the hotter the liquid. The amount of sulphate of lead dissolved is, however, small, and the fusing-point is only lowered about 5° , standing now at about 315° . At temperatures above its melting-point, it would be unjustifiable to call such a liquid an alloy, because its composition, in all probability, depends upon its temperature in as far as that composition is referred to the distribution of acids and bases. As it cools it gives up sulphate of lead in little crystals which sink. At the temperature of 315° general solidification begins, and is completed.

Of this alloy 4.2725 grams were treated with water and a little alcohol, and the insoluble sulphate of lead was found to weigh 0.1968 gram, corresponding to 4.61 per cent.

Sulphate of lead requires for fusion *per se* a bright red, almost white heat. But it is thus found to dissolve in hot fused nitre, and it separates as such on cooling the fused liquid. For the geological value of this fact see § 230.

§ 226. *Sulphate of Calcium* behaves in a similar manner. Highly refractory by itself, it dissolves in fused nitre. The cooling mixture, after shedding the excess of sulphate above that required for the eutectic alloy, solidifies at a constant temperature of about 315° . The lime, separated as oxalate and weighed as carbonate, showed a percentage of sulphate of 0.93. For 3.4832 grams of alloy gave 0.0238 gram of carbonate, or 0.03237 gram of sulphate.

§ 227. *Nitre and Sulphate of Barium*.—Even the sulphate of barium, which is typical of aqueous insolubility, dissolves in fused nitre, depressing the solidifying point, however, almost inappreciably. A little separates on cooling, and 8.54 grams of the eutectic alloy, when boiled with water, gave 0.0852 gram of the insoluble sulphate, or 0.98 per cent. It may be noticed in passing that, as is well known to analysts, sulphate of barium is soluble to an appreciable extent in another fused nitrate, namely nitrate of hydrogen.

§ 228. *Specific Gravity of the Eutectic Alloy of Nitrate of Potassium and Nitrate of Sodium*.

Slabs of nitre, nitrate of sodium, and the eutectic alloy of the two were cast upon a surface of cold metal, the liquids themselves being when poured only a few degrees above their melting-points. Their specific gravities were found by

weighing them in oil of turpentine of ascertained specific gravity. I found the

Specific gravity of nitre.....	2·2028
„ „ nitrate of sodium	2·0469
„ „ the eutectic alloy	2·1328

If the two were to mix without either gain or loss of volume in the proportion found in § 220, namely 32·9 of nitrate of sodium and 67·1 of nitrate of potassium, the specific gravity of the alloy would be 2·149. The density found shows that there has been an expansion on the two associating themselves together to form the alloy. And this expansion is presumably in near connexion with the lowering of the melting-point.

§ 229. The generalization of Berthollet is only one aspect of the question of distribution. When a compound body ax and another compound body by being brought together in watery solution give rise to an insoluble body ay and a soluble one bx , we have no more right to say that the change is brought about in virtue of the insolubility of ay than that it is due to the solubility of bx . Strictly speaking, it is due to the difference in solubility of the two. For the solubility of the one is as much concerned with the separation of the two new compounds as in the insolubility of the other. It is on this account that eutexia, without water, and as it exists in the case of two fused metals or anhydrous salts, may and must have a determining influence on the arrangement in ratio or kind of the constituents.

§ 230. *Geological and Mineralogical Significance of Eutexia.*—How the temperature of liquefaction of rocks may be lowered by the introduction of even small quantities of water will be discussed in my next memoir. It has been very diligently considered by Daubrée. Let us briefly examine the question of the interaction of rocks and their constituents, without, of necessity, the intervention of water.

In reviewing the analyses of Felspathic minerals, most of which, unless weathered after solidification, appear to be essentially anhydrous, we find them to be silicates of potassium and aluminum, in which, to use the common expression, the potassium is partly replaced by sodium, calcium, magnesium, and manganese, the aluminum by iron. That water is not

essential to the formation of this kind of mineral, is proved by the occurrence of it in copper and iron furnaces. Mica, on the other hand, appears always to contain water, sometimes as much as three or four per cent., with a lesser percentage of silica than felspar; it contains generally a far larger proportion of aluminum and of iron; the abundance of the latter element may indeed be considered, together with its deficiency in silica, as its distinguishing characteristic, chemically speaking, from orthoclase.

Silica—the great earth-acid, a title which it shares with carbonic acid, whose other realm is the air, and to some extent with hydrochloric acid, whose proper region is the sea—appears both in the anhydrous form and with as much as eleven per cent. of water. By its union with alumina it gives rise to clay, slate, and the minerals staurolite, andalusite, kyanite; with lime to Wollastonite; with magnesia (and iron) to bronzite; with lime and magnesia (and iron) to augite and diallage; with magnesia and iron (and lime) to hypersthene and olivine; with magnesia, lime, and iron to hornblende; with iron to Fayalite, and so on.

If, now, we adopt the often-asserted theory that variations in minerals belonging to the same class are brought about by the exchange of more or less of one base by another, the analyses land us in a difficulty, which seems insuperable. Let us suppose, for instance, that we have pure Wollastonite, consisting of

Silica	51·73,
Lime	48·27.

Replacing part of the lime by magnesia and iron, say 23·51 by 18·55 magnesia and 0·99 protoxide of iron, the silica rises to 55·15, and gives us an excellent example of augite (neglecting the manganese and alumina of that body).

	V. Bonsdorff.
Silica	54·83
Lime	24·76
Magnesia	18·55
Protoxide of iron	0·99
Protoxide of manganese . .	0·32
Alumina	0·28

But next let us examine hornblende, an analysis of which by V. Bonsdorff is given.

Silica	60·10
Magnesia	24·31
Lime	12·73
Protoxide of iron	1·00
Protoxide of manganese . .	0·47
Alumina	0·42
Hydrofluoric acid	·83
Water	·15
	<hr/>
	100·01

These bases, neglecting the water and hydrofluoric acid, require together 51·83 of silicic acid, instead of 60. No process of exchange of one base for another can make hornblende out of Wollastonite. It is essentially acid, unless in those varieties of amphibole which contain a considerable proportion of alumina; these, indeed, may be basic, acid, or neutral, according as the alumina is considered as a base saturating the silica, or an acid saturating lime or magnesia, or partly in the one predicament and partly in the other. As Wollastonite occurs along with amphibole and augite, there does not appear sufficient ground for this essential difference on the replacement theory.

I submit that, according to analogy, we should regard compound rocks and minerals, other than sedimentary rocks, as representing various kinds of eutectic alloys. We may for the sake of argument start from some known definite rock which is a true chemical compound, such as orthoclase, and trace the probable reactions between this and other rocks; or we may take a rock, like granite or syenite, of indefinite composition, and examine the probable assortment of its constituents on cooling. Starting with the melted mass, my experiments with salts have, I maintain, established that the clear molten granite will in cooling throw off as solids atomically definite salts, the last alloy to remain liquid being the eutectic alloy, which is constant only in composition in the sense in which such a body is so. It would follow therefore that the micas are the eutectic alloys of the proximate elements, or salts of

the melted granite. Quartz and felspar being both molecularly constituted, undergo solidification before mica. On account of the enormous effect which even a little water has in reducing the melting-point* and because silica is soluble in water, it is probable that the order of solidification is first felspar, and then quartz, and lastly mica. Quartz is thus speaking *en gros* pseudomorphic to felspar, and mica to both; all three are sometimes in this mass-sense pseudomorphic to slate, and mica is especially so. If fused nitre be saturated with nitrate of lead and sulphate of potash, and gradually cooled, sulphate of lead first separates, then sulphate of potash with sulphate of lead, then the eutectic alloy of all three. The sulphate of lead represents the felspar, the sulphate of potash with sulphate of lead represents the quartz, and the eutectic alloy represents the mica (see also § 38, Phys. Soc. Proc. 1874). Tourmaline and hornblende are probably both eutectic, whilst olivine is probably not.

§ 231. As to the great rock-masses themselves, if we assume that the earth is a drop of fused rock alloy with a solid crust, and that its history had been one of gradual undisturbed and symmetrical cooling, it is clear that, apart from sedimentary formations, the oldest solid rocks are those formed nearest the surface. But the disturbing causes are manifold: the earth-crust is under stress on account of the loss of volume on cooling. This strain is unequally distributed, on account of the want of sphericity of the earth's form, and on account of the centrifugal pressure towards the equator. Extra-terrestrial influences, such as the conjunction and apposition of the sun and moon and the variation in solar radiation, are asymmetrical, so that the earth's crust heaves and cracks and allows the eutectic melted alloy to break through, and as an intrusive mass metamorphose and overlies the older formations. Once rendered asymmetrical, the geographical features give rise to climates and weathers, and determine the formation of the sedimentary strata.

* See Daubrée, *Géologie expérimentale*. Also my next memoir, §§ 339-345.