Next the beautiful specimens of minerals which adorn our mineralogical cabinets generally form in the cavities or "vugs" as they are called in the rocks; beautiful crystals of iron at times occur also in the cavities in our steel ingots (Fig. 5); and in the same way we will often find most beautiful minute crystals of ice in the pear-shaped pipe of our common ingots of artificial ice.

Again, just as the crumpling of the rocks of the earth's crust produces what is known as a schistose structure, so we find such a structure (Fig. 6) in masses of iron when they have been crumpled in like manner.

Finally, gases evolved during solidification cause gas-bubbles or "blowholes" in ingots of ice and of steel, and also in glass (*A* and *B,* Fig. 4). These blowholes form at a time when the mass is still fluid enough to be pushed aside by the particles of gas evolved within it, so that these come together to form gas-bubbles; yet not fluid enough to permit these bubbles to rise by gravity to the upper surface and thus escape. So these bubbles remain entangled in the viscous mass.

4. Chemical Compounds Among Metals. — While the condition of the particles of pure metals which we find in our alloys calls for no special comment here, that of the chemical compounds and of the solid solutions requires a word.

The chemical compounds of one metal with another do not in general follow the law of valence, so that they are of the type known as "molecular." The law of valence retains its importance, but we must recognize that it is not a universal one. We may, however, make the important generalization that obedience to the law of valence is typical of a great number of our strong chemical compounds, those in which the atoms are powerfully united, yielding a compound which differs greatly in its properties from those of its components. And it is in accordance with this general idea that even the definite chemical compounds of one metal with another, as of copper with antimony, or gold with aluminium, or tin with antimony, as they do not follow the law of valence, are feebly combined, and that their properties differ from those of their component metals in a very much less degree than is the case with the common strong chemical compounds with which we are familiar in inorganic chemistry. The properties of water are wholly different from those of hydrogen and oxygen; the properties of common salt give no suggestion of

those of either chlorine or sodium. Naturally we find no such striking difference between the properties of a definite compound of aluminium with gold on one hand, and the properties of aluminium and of gold respectively on the other.

5. Solid Solutions. — What do we mean by this term? We use the word solution here to distinguish these substances from solid definite chemical compounds. We mean by solid solutions those solids which are to definite solid chemical compounds, like salt, what liquid solutions, like salt water, are to liquid definite chemical compounds, like pure water itself. We mean solids which have the essential characteristics of solutions so far as solidity itself permits.

To understand this let us ask what are the essential properties which distinguish our common liquid solutions from definite chemical compounds. In a definite chemical compound we have two essential features, (1) complete and absolute merging of the components into a new and different substance, chlorine and sodium losing their identity absolutely and forming a wholly different substance, common salt; and (2) a mathematically fixed ratio between the two components. In the case of solution, while this fixed-ratio feature is lacking, we have this same complete merging of the two substances. In a solution of water and alcohol we can neither by the microscope nor by any other means detect either the water or the alcohol; they unite to form a new substance: neither gravity nor centrifugal force separates them; the light alcohol does not rise to the surface, nor does the heavier water sink. This complete merging of their components and the absence of fixed ratio between those components, then, are the two essential characteristics of our common liquid solutions.

As the chemical forces which hold the dissolved bodies together in the new substance, the solution, are relatively feeble, naturally the properties of the solution do not differ markedly from the mean of the properties of the two bodies dissolved in each other.

Turning to the solid state we find in our glasses a similar state of affairs, except that the glasses are solid while common solutions are liquid. The silica, lime and alkali of the glass are absolutely merged; neither the microscope nor any other means enables us to detect either silica or lime or alkali as a separate en-

tity in the glass, so long as it remains a glass. Only when we destroy it, tearing it asunder by analysis, can we detect any of its components. We have then in the glass a chemical merging of the components; but it is in indefinite ratios. The percentage of silica or of lime can vary by infinitesimal gradations from specimen to specimen, and this variation is accompanied by corresponding progressive change in the physical properties. The change from specimen to specimen, then, both in composition and in properties, is per gradum; whereas the changes from one definite chemical compound to another, from water to hydrogen peroxide for instance, are per saltum. The glasses then have these two essentials of solutions, the substances present are (1) completely merged, but (2) in indefinite proportions.

In the same way many of our metals, as it were, dissolve in each other, and we find them in the solidified state completely merged in each other, forming alloys which differ from specimen to specimen by infinitesimal gradations, and yet the component metals cannot be distinguished in the alloy by the microscope or by any other means. The separate individual existence of each has ceased. Here then we have the essential characteristics of solutions, *viz.*, (1) complete merging of the components (2) in indeterminate proportions; and on this account we give to these substances the name " solid solutions."

And just as the properties of the liquid solution, its color, density, electric conductivity, *etc.*, do not differ markedly from those of the mean of its components, so we find that the physical properties in general of those alloys which are solid solutions do not differ markedly from the mean of the properties of the metals which compose them.*

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* The author has found this conception of solid solutions so hard for many students to grasp that, for their sake and at the risk of seeming to most readers needlessly explicit, some further discussion, line upon line, seems desirable. When chlorine and sodium unite to form salt, the two elements lose their identity completely, they are completely merged. A wholly new substance arises, salt, having little resemblance to either of its components. They have become one; they cannot be separated or distinguished from each other so long as they are united. Neither the microscope nor gravity nor centrifugal force nor any other purely mechanical force separates them or enables us to distinguish one from the other. It is this complete sinking of their individual identity, this birth of a new substance, in which neither of the component sub-

6. Isomorphous Mixtures and Mixed Crystals. — Solid solutions are called by some " isomorphous mixtures " and by some " mixed crystals." The term " isomorphous mixtures " would naturally be suggested by the fact that the familiar cases of two definite inorganic compounds which crystallize together to form homogeneous crystals, the molecules of each substance practically entering into and completely identifying themselves with the molecules of the other, are cases in which the two substances are isomorphous, *i. e.,* when by themselves they yield crystals of the same form, *i. e.,* " isomorphous " crystals. This property then of two different substances of merging their existence completely in single crystals, is one which we associate with isomorphous bodies, and this association easily leads to applying the word " isomorphous " to all cases of such identification and merging. But reflection shows us that the similarity of crystalline form, even were it not only a constant concomitant but

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stances is distinguishable by any means whatever so long as this new substance remains undecomposed — it is this that we here call merging.

If we grind silica and magnetic iron oxide to the most impalpable powder and mix them with most extreme thoroughness, they still remain two distinct bodies, silica and iron oxide, merely intimately mixed mechanically. We can again separate them by appropriate mechanical means. Under a sufficiently powerful microscope we can still see the white particles of silica and the black ones of iron oxide. If we immerse them in a liquid heavier than the silica but lighter than the iron oxide, we separate them by gravity, the silica gradually rising to the top, while the iron oxide sinks to the bottom. Or we can separate them by means of a magnet.

But let us melt them together, and they unite and merge, they become one, and neither can now be distinguished by any means, nor separated mechanically from the other, so long as this merging remains.

Suppose that we have a room cooled to — 40° C.; that in this we grind up ice and crystals of hydrated cupric sulphate (blue vitrol) quite as we ground up our silica and iron oxide; to simplify our ideas suppose that at this temperature the cupric sulphate and ice do not react on each other but remain separate quite as the silica and iron oxide do, and that we then mix them in a bottle with extreme thoroughness. They still constitute simply an intimate mechanical mixture; they are not merged; by sufficient magnification we can see under the microscope the transparent white particles of ice and the blue ones of cupric sulphate. By carefully tapping the bottle we can induce the heavy crystals of cupric sulphate to work their way down to the bottom of the bottle, leaving the lighter particles of ice above. Now let us heat the whole over the lamp, and soon the ice melts and dissolves the cupric sulphate. Now in this solution

a necessary condition of this merging, is clearly not its essence. We see no conclusive reason why two metals of different crystalline forms should not completely merge. Their union could not properly be called isomorphous, but it would properly be called a solid solution.

The chief reason, however, for preferring this latter term is that it is based, not on what could at most be a concomitant or necessary condition, but on the essential properties of this class of substances, the fact that they have all the prominent essential properties of aqueous solutions save their fluidity.

As to the expression "mixed crystals" it seems most unfortunate, because it is so liable to mislead, for it certainly would suggest to many a mechanical mixture. For instance, silver and gold dissolve in each other in all proportions, and the crystals of the two metals thus merged are spoken of by some as mixed crystals of silver and gold. This certainly will suggest to many that the mass is a conglomerate, a mechanical mixture of particles

we have no longer a mechanical mixture but absolute merging, merging as complete and as little broken up by mechanical means, as little capable of being resolved by the microscope, as the merging of our chlorine and sodium in salt or of our silica and iron oxide in our iron silicate.

Of course, we can by appropriate chemical means break this solution up; we can insert a sheet of metallic iron and precipitate the copper on it; we can break the solution up chemically; but so long as it remains a solution, the water and the cupric sulphate lack their independent existence as two separate entities mechanically mixed, and now form one entity different from either of its components. We may dispute as to the nature of this new entity, as to the nature of solutions; we may regard them as composed of ions or whatever we please; but that the solution is one whole, that in it the water and the cupric sulphate have merged their separate existence and have coalesced to form some kind of a new thing, and some one new thing, cannot be doubted. Let us leave out of sight completely our conceptions of the nature of solutions, and for the present satisfy ourselves with this idea of (1) the complete merging of the separate existence of the two components, the water and the cupric sulphate, in this new thing, the solution, (2) in indefinite ratios.

When we find that the constituents of a solid, such as the silica, lime and alkali of a glass, or the gold and silver of a silver-gold alloy, have thus completely merged and sunk their separate individual existence in this one new body, the glass or the alloy; and when we find that the composition of this solid is not in definite chemical ratio but differs by infinitesimal gradations from specimen to specimen, we say that it has the essential characteristics of a solution so far as those characteristics are compatible with solidity itself; and we call the mass a solid solution.

of pure gold and particles of pure silver, which is exactly the opposite of the truth. Indeed, whether we speak of isomorphous "mixtures" or of "mixed" crystals, the idea of mixture leads the mind rather away from than towards the conception of merging, which is the essence of the matter; while "solution" in itself suggests merging.

7. Solid Solutions may be Heterogeneous. — Liquid solutions, as we know, are habitually homogeneous, because in the liquid state diffusion takes place with considerable rapidity, so that even if a solution is initially heterogeneous, diffusion tends to make it homogeneous. From the conditions under which they form, however, and from the slowness of diffusion in the solid state, we should expect solid solutions to be heterogeneous. (See § 55, p. 66.)

8. Methods of Study of the Constitution of Alloys. — As the science of petrography was in an advanced stage when that of metallography, of the constitution and structure of metals, was in its infancy, we naturally ask why the methods so fully developed for petrography have not been applied to metallography.

We may say that the essential procedure in petrography is to recognize the minute or even microscopic crystalline grains in our rock-masses by examining them with the microscope and with the polariscope, and by finding that they have the same crystalline form, and the same effect on polarized light, as the large crystals of the same minerals with which we are already familiar in the form of our cabinet specimens. Having determined accurately the crystalline form of quartz and its effect on polarized light by the study of large-sized cabinet crystals, we are able to recognize minute or even microscopic crystals of quartz by finding that they have the same crystalline form and the same action on polarized light. Manifestly, this method is wholly inapplicable to metallography. In the first place there are very few metals and alloys of which we have cabinet specimens suitable for standards with which to compare the crystalline form or other properties of the microscopic crystals which we find in our alloys.

Moreover, the metals and their alloys are opaque, so that the polariscope is wholly inapplicable. The discovery of the X-rays may have given rise to the hope that by them we could meet the difficulty of the opacity of our metals; but reflection

shows that this hope was vain. For in most cases the particles of the different components of our alloys are so exceedingly minute that any individual grain of crystal would occupy but an insignificant fraction of the thickness even of the thinnest possible section, so that any given X-ray, in passing through such a section, would pass not through one individual grain or crystal of a given component, but through many different superposed crystals of all the different components which were present. In this way the shape of each one would be completely obscured and eclipsed by that of the others, and the effect of any given particle upon the X-rays would be masked by the effect of the other crystals through which that same ray would pass. There are indeed a few cases in which the individual crystals are large enough to be thus outlined by the X-rays, but even in these cases the structure can be more readily detected by microscopic study of the surface after it has been properly prepared. Thus the X-ray method is without either present or prospective value.

The chief method actually used in metallography is to correlate the results of our examination (1) of the structure as revealed by the microscope, (2) of the physical properties of individual alloys, and (3) of the physical properties of series of alloys taken as a whole. The meaning of this third method I will make clear later. We will now take up these three methods of research consecutively.

9. MICROSCOPIC EXAMINATION.* — Many of our alloys, as has been already pointed out, have a granitic or porphyritic

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*A. Sauveur, "Microscopical Examination of Iron and Steel," *Engineering and Mining Journal,* LXIV, p. 215.

A. Sauveur, "Mechanical Uses of the Science of Metallography," *Engineering Magazine,* XVII, p. 977.

Stead, "A Practical Lesson in the Preparation of Metal Sections for Microscopic Examination," *Proceedings South Staffordshire Institute,* Session 1896-97, XII, p. 2.

Stead, "Practical Metallography," *The Metallographist,* III, p. 220.

F. Osmond, "Méthode Générale pour l'Analyse Micrographique des Aciers au Carbone," *Bulletin Société d'Encouragement pour l'Industrie Nationale,* May, 1895. See preferably the reprint in the "Contribution à l'Étude des Alliages, Commission des Alliages," 1896-1900, p. 277.

F. Osmond, "La Métallographie Considérée comme Méthode d'Essai," *Baumaterialienkunde,* II, No. 4.

Sir Wm. Roberts-Austen, "On Photomicrography of Steel Rails,"

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structure; that is to say, like a granite they are composed of distinct grains, each grain being some one distinct entity, and of a distinct mineral species; and the different grains are of two or more different species. In the case of common granite there are grains of three different mineral species, mica, quartz and feldspar, lying side by side; and any individual grain is of some one of these species.

Now, the composition of granite taken as a whole is indeterminate, in the sense that, if we take a series of different granites and determine their ultimate composition, we find that the percentage of silica or of lime varies by irregular gradations from one specimen to the next; and the percentage of these components might vary by infinitesimal gradations from one granite to the next. But, though the composition of granite is in this sense wholly indeterminate, and though there is thus no possible composition of which we may say "This is the true composition of granite"; yet each of the several minerals which compose the granite, the mica, quartz and feldspar, is a perfectly definite chemical compound with definite physical properties.

So many of our alloys are granitic or porphyritic. They are found by the microscope to consist of grains or crystals of different definite substances. Each grain is of some one of these substances, and these different unlike grains lie side by side, like the mica, quartz and feldspar of a granite. The substances which compose these different grains in our granitic or porphyritic alloys may be (1) pure metals,* or (2) definite chemical compounds of two or more metals with each other in rigidly fixed atomic proportions, such as aluminide of gold ($AuAl_2$), antimonide of copper (Cu_2Sb_3?) and antimonide of tin ($SnSb$), compa-

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Institution of Civil Engineers, January 17, 1899, *Proceedings,* CXXXVI, p. 174.

Le Chatelier, "La Technique de la Métallographie Microscopique," "Contribution à l'Étude des Alliages, Commission des Alliages," 1896-1900, p. 421.

*Pure metals are spoken of for simplicity, serving as a type; it is probable that, in most granitic alloys, the particles which may at first appear to be pure metals are in fact not quite pure; but that each apparently pure metal contains, dissolved in itself, a little, and perhaps a very little, of each of the other metals present.

rable with the chemical compounds with which we are familiar in common inorganic chemistry; or (3) definite chemical compounds of a metal with a metalloid, such as the iron carbide (Fe_3C) called *cementite*, which plays a very important part in the metallography of iron and steel; *etc., etc.* One aim of microscopic examination is to ascertain whether the alloy is of this porphyritic type and consists of different distinct crystals of definite chemical composition, or whether it is of the obsidian type consisting solely of a solid solution; or whether it contains both definite minerals and also solid solutions. The further aim is to distinguish the shape, size and the properties both physical and chemical of these various components.

The first step in general is to polish the metallic mass so that a large field may be visible under high magnification. The second is to subject it to an attack, either chemical or mechanical, which will affect the different constituents in different ways, and thus enable us not only to distinguish one from another but also to determine the shape, habit and properties of each. Of these methods five deserve mention here. Of these the first three are chemical, the fourth mechanical, and the fifth partly chemical and partly mechanical. They are as follows:

(a) *Simple attack* by some solvent such as nitric acid, iodine or licorice, a method which we owe to Sorby.* Such a method may dissolve away one component more than another, or color one component differently from another, or it may simply eat away the joints between adjacent grains of crystals, and thus disclose their shape when they are later examined under the microscope.

(b) *Weyl's Method*, which has received great development in the hands of Charpy, is to attack by means of a solvent under the influence of a very gentle electric current. Charpy uses as the two poles (1) the alloy which is under examination and (2) at times platinum and at times another alloy of a composition so nearly similar to the first that the electro-motive force shall be very feeble, and therefore that the attack shall be extremely gentle. This gentleness is needed in all our methods. The particles which we wish to recognize and identify are so extremely minute, and often so feebly held in place, that we must use the

* *Journal Iron and Steel Institute*, 1887, I, p. 256.

utmost gentleness, whether in dissolving or in mechanically separating one from the other, lest we remove mechanically those components which we seek to leave untouched.

(c) *Heat-Tinting*. The different constituents may be differently colored by gently heating the polished surface, so that the more oxidizable ones become covered with oxide tints. This method has been used by Guillemin, and later by Stead,* with most valuable results.

(d) *Relief Polishing*. Beyond these we have the mechanical methods, of which Osmond's "relief-polishing" is very important. By prolonged very gentle polishing, the softer constituents of a conglomerate alloy are worn away, leaving the harder ones standing in relief.†

(e) *Osmond's "attack-polishing"* combines the chemical and mechanical methods happily. He polishes the surface while it is exposed to a reagent which attacks or colors the different constituents differently, so that disintegration by the reagent and removal by the rubbing go hand in hand.

CHAPTER II. — COOLING CURVES

10. Physical Properties of Individual Alloys. Cooling Curves. — If we were studying the alloys of two metals, such as the alloys of silver with gold taken as a group, or those of lead with tin taken as a group, we should of course examine many of these alloys individually, in order to see to what degree it had the property toward which our study was particularly directed, be it hardness, tensile strength, conductivity, or whatever. But besides this, in order to learn the constitution of that individual alloy, we should in particular determine with great care its "cooling curve." Let an example explain what a cooling curve is. If we place a thermometer in a flask of pure water, and place that water in a freezing-mixture, and follow carefully the fall of

* *Journal Iron and Steel Inst.*, 1900, II, p. 137.
† F. Osmond, "Méthode Génerale Pour L'Analyse Micrographique des Aciers au Carbone," *Bulletin de la Société d'Encouragement*, May, 1895. See preferably the reprint in the "Contribution à l'Étude des Alliages," 1896-1900, p. 277.