freezing point curve, and then travels along it till the non-variant point is reached. In this way two temperature points are obtained in the investigation—the higher giving a point on the equilibrium curve, the lower showing the non-variant point.

Other pairs of alloys, showing more complicated relations, are described in Alloy. Experiments on alloys are, in some ways, easier to make than on pairs of non-metallic substances, partly owing to the possibility of polishing sections for microscopic examina­tion, and the investigation of alloys has done much to elucidate the general phenomena of solution, of which metallic solution constitutes a special case.

When the two components form chemical compounds with each other, the phenomena of mutual solubility become more complex.

For a simple case to serve as an introduction, let us again turn to alloys. Copper and antimony form a single compound SbCu2. If either copper or anti­mony be added to this compound, the freezing point is lowered just as it would be if a new sub­stance were added to a solvent. Thus on each side of the point B representing this compound, the curve falls. Proceeding along. the curve in either direction, we come to a non-variant or eutectic point. In one case (represented by the point A in the figure) the solid which freezes out is a conglomerate of crystals of the compound with those of antimony, in the other case C with those of copper. Thus in interpreting complicated freezing point curves, we must look for chemical compounds where the curve shows a maximum, and for a eutectic or cryohydrate where two curves meet at a minimum point.

We are now ready to study a case where several compounds are formed between the two components. A good example is the equilibrium of ferric chloride and water, studied by B. Roozeboom. The experi­mental curve of solubility is shown in fig. 7. At A we have the freezing point of pure water, which is lowered by the gradual addition of ferric chloride in the manner shown by the curve AB.. At B we have the non-variant cryohydric point at which ice, the hydrate Fe2Cl6∙i2H2O, the saturated . solution and the vapour are in equilibrium at 55°C. As the proportion of salt is increased, the melting point of the con­glomerate rises, till, at the maximum point C, we have the pure compound the hy­drate with twelve molecules of water. Beyond C, the addition of salt lowers the melting point again, till at D we obtain another non-variant point. This indicates the appearance of a new compound, which should exist pure at E, the next maximum, and, led by these considerations, Roozeboom discovered and isolated a previously unknown hydrate, Fe2Cl67∙H2O. In a similar way the curve FGH, between 30° and 55°, shows the effect of the hydrate Fe2Cl6∙sH2O, and the curve HJK that of the hydrate Fe2Cl6∙4H2O, which, when pure, melts at 73∙5°—the point J on the diagram. At the point K, 66°, begins the solubility curve of the anhydrous salt, Fe2Cl6, the fusion point of which when pure is beyond the limits of the diagram. Let us now trace the behaviour of a solution of ferric chloride which is evaporated to dryness at a constant temperature of 31°. The phenomena may be investigated by following a hori­zontal line across the diagram. When the curve BC is reached, Fe2Cl6∙12H2O separates out, and the solution solidifies. Further renewal of water will cause first liquefaction, as the curve CD is passed, and then resolidification to Fe2Cl6∙7H2O when DE is cut. Again the solid will liquefy and once more become solid as Fe2Cl6∙5H2O. Still further evaporation causes these crystals to effloresce and pass into the anhydrous salt. As we have seen, the maxima of the various curve-branches at C, E, G, and J corre­spond with the melting points of the various hydrates at 37 , 32∙5°, 56° and 73∙5° respectively; and at these points melting or solidifica­tion of the whole mass can occur at constant temperature. But we have also found this behaviour to be characteristic of the non- variant or transition points, which, in this case, are represented by the points B,D,F,H and K (-55°, 27·4°, 30°, 55° and 66°). Thus in two ways at least a constant melting point can be obtained in a two-component system.

*Solid Solutions.—*In all the cases hitherto considered, the liquid phase alone has been capable of continuous variation in composition. The solid phases each have been of one definite substance. Crystals of ice may lie side by side with crystals of common salt, but each crystalline individual is either ice or salt; no one crystal contains both components in proportions which can be varied continuously. But, in other cases, crystals are known in which both components may enter. Such pheno­mena are well known in the alums—double sulphates of alu­minium with another metal. Here the other metal may be one, such as potassium, or two, such as potassium and sodium, and, in the latter case, the proportion between the two may vary continuously throughout wide limits. Such structures are known as mixed crystals or solid solutions.

The theoretical form of the freezing point diagrams when solid solutions are present depends on the relation between the available energy and the composition in the two phases. This relation is known when the amount of either component present in the other is very small, for it is then the relation for a dilute system and can be calculated. But at intermediate compositions we can only guess at the form of the energy-composition curve, and the freezing point composition curve, deduced from it, will vary according to the supposition which we make. With the. most likely forms for the energy curves we get the accompanying diagrams for the relation between freezing point and concentration.

It will be noticed that in all these theoretical curves the points of initial fusion and solidification do not in general coincide; we reach a different curve first according as we approach the diagram from below, where all is solid, or from above, where all. is liquid. Again, it will be seen that the addition of a small quantity of one component, say B, to the other, A, does not necessarily lower the melting point, as it does with systems with no solid solutions; it is quite as likely to cause it to rise. The second and third figures, too, show that the presence of solid solutions may simulate the phenomena of chemical combination, where the curve reaches a maximum, and of non-variant. systems where we get a minimum. The fourth figure shows that, in some cases, it should be possible for solid solutions to be present in a limited part of the field only, being absent between the two nearly vertical lines in fig. 11. Experiment has revealed the existence of systems in which these phenomena are displayed. As an example we may take the case of mixtures of naphthalene and B-naphthol, substances which form solid solutions in each other. The freezing and melting point curves are exactly similar to theoretical curves of fig. 8, the point A representing pure naphthalene and B pure B-naphthol. When the equilibria become more complex difficulties of interpre­tation of the experimental results often arise. It is often very difficult to distinguish between a chemical compound, for example, and the case of solid solution represented by fig. 9. All available evidence, from the freezing point curve and from other sources must be scrutinized before an opinion is pronounced. But the elucida­tion of the complicated phenomena of solid solutions would have been impossible without the theoretical knowledge deduced from the principle of available energy.

*Supersaturation.—*When a crystal of the solid phase is present the equilibrium of a solution is given by the solubility curves we have studied. If, however, a solution be cooled slowly past its saturation point with no solid present, crystallization does not occur till some lower temperature is reached. Between the saturation point and this lower temperature, the liquid holds in solution more of the solute than corresponds with equilibrium, and is said to be supersaturated. A familiar example is to be found in solutions of sodium sulphate, which may be cooled much below their saturation point and kept in the liquid state till a crystal of the hydrate Na2SO4∙10H2O is dropped in, when solidifi­cation occurs with a large evolution of latent heat. These phenomena are explicable if we consider the energy relations,