

SOLID SOLUTIONS

BY HAMILTON P. CADY

No complete freezing-point curves have hitherto been determined for systems in which two series of solids solutions occur. Owing to the ease of analysis naphthalene and monochloroacetic acid¹ seemed a good system to investigate. The naphthalene used in these experiments was purified by repeated crystallization from aqueous alcohol and melted sharply at 79.9° . The monochloroacetic acid was purified by fractional distillation. It boiled at about 185° and melted at 62° . The following method was used in preparing and separating the solid solutions. By preliminary experiments it was determined what amounts of acid and naphthalene should be taken in order to get suitable amounts of the solid and liquid phases at each temperature. A mixture of acid and naphthalene was then melted and placed in the apparatus shown in Fig. 1.

In the diagram, A is a funnel which held the melted mixture and in which the crystallization took place; C is a stirrer; D is a glass stopper for closing the bottom of the funnel until it was time to draw off the liquid; E is an asbestos filter; F a glass tube sealed to the stem of the funnel so that this latter can be kept warm to the very tip; H a tube containing soda-lime. The whole apparatus was jacketed with a water-jacket B kept at a constant temperature by the method previously described.² The solution was kept for several hours at the desired temperature and stirred frequently. At the end of the experiment the liquid portion was sucked off by means of a filter pump. The

¹ Some unpublished measurements made in Leipzig by Mr. Buckingham seven years ago had made it probable that these two substances formed two series of solid solutions.

² Jour. Phys. Chem. **2**, 242 (1898).

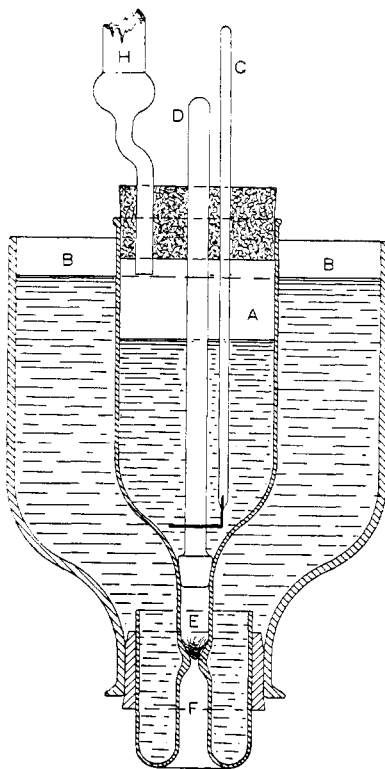


Fig. 1

temperature was then raised until the solid solution liquefied and the melt was filtered off. The two filtrates were analyzed by taking weighed portions and titrating the acid with potassium hydroxid solution. The naphthalene was determined by difference. There was no difficulty in dissolving the acid out of the naphthalene by means of water. On shaking the solid mass with water hot enough to melt it, the acid went into solution in a very short time. If the crystals were finely pulverized, cold water would remove all the acid very quickly. In fact no difference could be detected qualitatively between the rate at which the acid dissolves from a finely powdered solid solution of naphthalene and monochloroacetic acid and that at which it dissolves from a mechanical mixture of the same two substances. In this

respect these solid solutions differ markedly from those in which barium sulfate is one of the components. In spite of the solubility of barium chlorid in water, it can only be washed out with incredible slowness from precipitated barium sulfate. In separating monochloroacetic acid from naphthalene, it is advisable not to use hot water any more than is absolutely necessary, otherwise there will be a secondary reaction forming glycolic and hydrochloric acids.

The analytical results expressed in grams per hundred of the two components are given in Table I, the data for the fusion curve along which the crystals are chiefly naphthalene being given under the heading of 'naphthalene series', while the data for the other fusion curve are given under 'acid series'.

TABLE I
Naphthalene series

Temp	Solid solution		Liquid solution	
	Naph	Acid	Naph	Acid
75°	96.6	3.4	84.4	15.6
70	95.4	4.6	69.7	32.3
65	89.2	10.8	53.3	46.7
60	80.3	19.7	42.4	57.6
55	59.6	40.4	31.3	68.7
53.5	29.4	70.0
Acid series				
60°	1.7	98.3	4.0	96.0
55	2.1	97.9	21.0	79.0

These results are shown graphically in Fig. 2. AC and BC give the compositions of the saturated solutions. AD gives the compositions of the solid solutions containing an excess of naphthalene and BE the compositions of the crystals. By the ordinary method it is of course impossible to determine the composition of the solid phases at the quadruple point because a mixture of the two phases separates. The temperature at this point is 53° and the liquid solution contains 71.3 percent acid to 28.7 percent naphthalene. The curve BE is so nearly a straight line that no serious error will be made by extrapolating

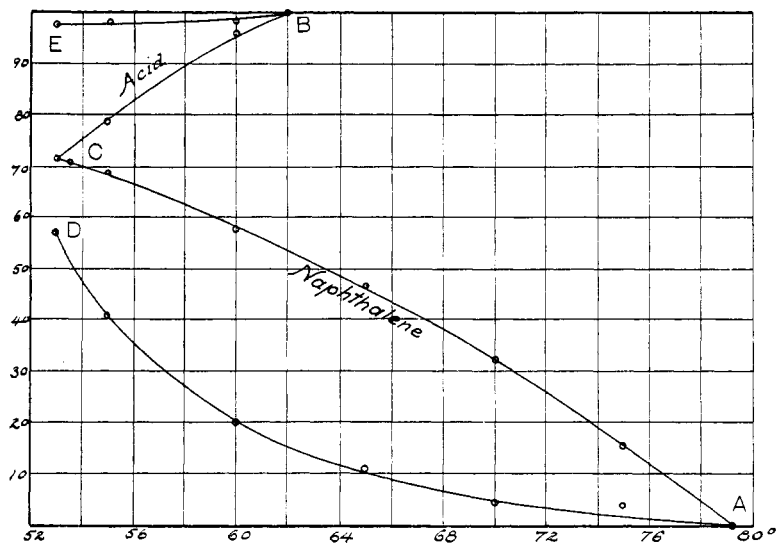


Fig. 2

and taking the composition of the crystals as 97.5 percent acid and 2.5 percent naphthalene. On the other hand the curvature of AD is such that an extrapolation from 55° to 53° is not necessarily very accurate. An attempt was therefore made to determine the limiting composition by the following method. Different mixtures of naphthalene and acid were allowed to solidify and then examined under the microscope. When the mixture contained fifty percent of acid or less there was only one kind of crystal. With sixty percent of acid two kinds of crystals could be detected. We may therefore consider 57 percent of acid as being very near the truth.

It was thought possible that acetic acid might also form solid solutions with naphthalene, but a few experiments showed that this was not the case and that the two substances crystallize without admixture. No experiments were made with monobromacetic acid because it seemed reasonably certain that this substance would behave like monochloracetic acid. On the other hand it seemed of interest to make some qualitative experiments with glycolic acid to determine whether the replace-

ment of hydrogen by hydroxyl would tend to make solid solutions possible. The glycolic acid was made from monochloroacetic acid and was not entirely free from water. In spite of the traces of moisture very considerable quantities of acid dissolved in the solid naphthalene. At 74.5° the solid phase contained 18.7 percent acid as against 3.38 percent monochloroacetic acid at 75° or 4.61 percent at 70° . Experiments were also made with malonic and succinic acids; but these acids are so sparingly soluble in melted naphthalene that there was practically no lowering of the freezing-point and it was impossible to make measurements. We may conclude therefore that malonic and succinic acids do not form solid solutions with naphthalene.

It was noticed that the glycolic acid could not be washed out readily from the naphthalene; it being necessary to melt the latter in order to effect a separation. In this respect it resembles the solid solutions formed with barium chlorid and barium sulfate.

Since the time of van 't Hoff's paper on solid solutions¹ it has been clear that the solute lowers the vapor-pressure of the solid solvent; but there have been reasons for supposing that the relation between concentration and lowering of the vapor-pressure was not the same quantitatively for the solid and for the liquid solutions. Küster² pointed out that, according to the theory, the freezing-point should remain unchanged when the solid and liquid solutions had the same composition. This, however, is not the case for many isomorphous mixtures and for this reason Küster proposed to classify isomorphous mixtures as something different from solid solutions. Walker and Appleyard³ found that the reacting weight of picric acid in silk as determined by applying Nernst's distribution law to the system, silk, water and picric acid, was less than the reacting weight in water. This struck them as so improbable that they decided that picric acid and benzene did not form a solid solution. Küster⁴ obtained even more surprising results with the system, iodine, starch and

¹ Zeit. phys. Chem. **5**, 322 (1890).

² Ibid. **12**, 510 (1893).

³ Jour. Chem. Soc. **69**, 1334 (1896).

⁴ Liebig's Annalen, **283**, 360 (1894).

water, the apparent reacting weight of the iodine in the starch being only one-fifth of the value in water. There seems no good reason for denying the existence of solid solutions in all three of these cases. By definition a solid solution is a solid phase whose composition can vary continuously within certain limits.¹ Isomorphous mixtures certainly come under this head. To make a qualitative classification on the basis of the applicability or non-applicability of a quantitative theorem such as the van't Hoff-Raoult formula is putting the cart before the horse. The distinctions made by Küster and by Walker and Appleyard are also bad in that the phases which are cast out of the ranks of the solid solutions are not taken in anywhere else and remain as waifs and strays. The only conclusion which does not go beyond the facts is that in certain cases of solid solutions that have been examined, the van't Hoff-Raoult formula for the change of the partial pressure with the concentration does not hold—as usually applied. The next step is to try to find out what the disturbing factor is.

For isomorphous mixtures we know that the formula, as usually applied, does not hold. It is not known whether it applies in the case of systems where two series of solid solutions are possible. Owing to the low vapor-pressures of such systems, direct measurements present very unusual difficulties. It is possible in some cases to obtain an approximate result by an indirect method. The effect of the separation of a solid solution is to raise the apparent freezing-point of the liquid solution. In case a solid solution does not separate the lowering of the freezing-point can be calculated approximately by means of the formula $K_1 \Delta T = \frac{n}{N-n}$. The difference between this calculated freezing-point and the actual freezing-point gives the rise of freezing-point due to the solid solution. According to the van't Hoff formula, as ordinarily applied, the same formula that had been used to calculate the lowering of the freezing-point should

¹ Bodländer has written an excellent statement of our knowledge in regard to solid solutions. *Jahrbuch für Mineralogie, Geologie und Palaeontologie, Beilage-Band*, 12, 52 (1898).

describe the relation between the rise of freezing-point and the concentration of the solid solution. It is clear that this method is not very accurate. It assumes that the lowering of the freezing-point can be calculated with accuracy in case no solid solutions occur. This is not strictly true for any solutions over any considerable range of temperature and does not hold at all for many solutions, such as alcohols or oximes in benzene. The assumption is also made that the reacting weight is 'normal' in the two solutions and there is the further assumption that the heat of fusion is unchanged. Then, too, the rise of freezing-point is the difference between two other values and contains a relatively large percentage error. For this reason the results by this method can never be very satisfactory, though they may be instructive.

The observations with naphthalene and monochloroacetic acid have been calculated on this basis, as being the only data available. If ΔT is the depression of the freezing-point calculated on the assumption of no solid solution, and $\Delta T'$ is the observed lowering of the freezing-point, the rise $\Delta T''$ due to the solid solution will be given by the equation $\Delta T - \Delta T' = \Delta T''$. The results of the calculations for the naphthalene series are given in Table II. The constant used in calculating ΔT was 0.0183, and the K in the fifth column is that calculated, taking $\Delta T''$ and the concentrations in the solid phase as given.

TABLE II
Naphthalene series

Temp	ΔT	$\Delta T'$	$\Delta T''$	K_1
75°	10.9°	4.9°	6.0	0.0075
70	20.0	9.9	10.1	0.0061
65	29.8	14.0	14.9	0.0095
60	35.8	19.9	15.9	0.0157
55	40.8	24.9	15.9	0.0300

It will be noticed that K_1 is in no sense of the word a constant; but it would be unsafe to draw the conclusion that the van 't Hoff-Raoult formula did not apply to the solid solutions of monochloroacetic acid in naphthalene. The range of temperatures

is nearly twenty-five degrees and it is doubtful whether the formula would apply to any system under such circumstances. Acetic acid gives abnormal results in benzene and presumably in naphthalene and there is no reason to suppose that monochloroacetic acid does not do the same. For this reason the calculated values for ΔT are unquestionably too large and the same is true for $\Delta T''$. Decreasing $\Delta T''$ would make the values of K diverge more than they now do; but, on the other hand, if we are to assume polymerization in the liquid solution there is certainly no reason why a similar state of things should not occur in the solid phase. It must be admitted that this is an exceptionally bad case from which to make deductions and that the most one is justified in saying is that it has not been possible to confirm the van 't Hoff-Raoult formula.

The results with the acid series are equally unsatisfactory. The value of the constant was 0.0173, the heat of fusion being taken from Pickering's data.¹ For the first observation the actual lowering of the freezing-point is slightly greater than that calculated on the assumption of no solid solution, a result doubtless due to experimental error. For the other observation the rise of the freezing-point $\Delta T''$ is roughly twice what it should be. In the first three observations in Table II the values for K_1 are not over half what they should be, meaning that the rise of freezing-point as calculated is not less than twice as great as that required by the theory. If we try to account for this by assuming that the error is in ΔT , we are placed in the unpleasant position of having to assume very considerable polymerization in the liquid phase in order to get 'normal' results in the solid phase. In view of the fact that in all cases of isomorphous mixtures the rise of the freezing-point is greater than that required by the formula, it is probable that one may make the generalization that in solid solutions the lowering of the partial pressure is always greater than could be predicted from the van 't Hoff-Raoult formula in its usual form. To assume dissociation in order to account for this would be ridiculous.

¹ Jour. Chem. Soc. 67, 664 (1895).

Although it is not possible at present to treat the subject quantitatively, for lack of sufficient data, it is easy to show qualitatively that the van't Hoff-Raoult formula could not be expected to apply to solid solutions save in very exceptional cases. The deduction of the formula $\frac{n}{N} = \log \frac{p}{p_0}$ is the same for a solid as for a liquid solution and contains the explicit assumption that the heat of dilution is zero. In the case of liquid solutions the heat of dilution may be so great as to reduce the apparent molecular weight nearly to half the normal value, as for instance with the amalgams of the metals of the alkalis and of the alkaline earths.¹ We know nothing about the heat of dilution of solid solutions; but there is no reason to suppose that it is zero in the large majority of cases. Whenever it is not zero the formula of van't Hoff-Raoult for the change of partial pressure with concentration will not apply unless a correction be applied for the heat of dilution. Another factor that has been completely disregarded by Küster and others is that the heat of fusion of the solid solution is not that of either pure component. We see therefore that there is no reason why the change of pressure with concentration in solid solutions should follow the simple van't Hoff-Raoult formula. It is also obvious that all determinations of reacting weights in solid solutions are liable to very considerable errors, errors of such extent as practically to vitiate all conclusions drawn from them—for the present.

This research has been carried on under the direction of Professor Bancroft. The chief results are:

1. Naphthalene and monochloroacetic acid form two series of solid solutions.
2. The data necessary for the construction of the concentration-temperature diagram have been determined.
3. Glycolic acid forms two series of solid solutions with naphthalene and is much more soluble in naphthalene than is monochloroacetic acid.

¹ Ramsay. Jour. Chem. Soc. **56**, 521 (1889). Cf. Cady. Jour. Phys. Chem. **2**, 525 (1898).

4. Acetic acid does not form solid solutions with naphthalene and it is probable that malonic and succinic acids do not.

5. It is probable that for most solid solutions $\frac{n}{N} < \log \frac{p}{p_1}$.

6. The cause of this discrepancy is to be sought in the heat effects.

Cornell University