XC.—*Studies on Hydrogen Cyanide. Part III. The Freezing Points of Hydrogen Cyanide–Water Mixtures.*

By JOSEPH EDWARD COATES and NORMAN HOLT HARTSHORNE.

GAUTIER (*Ann. Chim. Phys.*, 1869, **17**, 103) determined the "melting points" of a series of frozen mixtures of hydrogen cyanide and water. His curve, drawn through ten points only, exhibited a minimum at $-22{\cdot}5°$ and a break (concave to the composition axis) at $-16{\cdot}2°$, at the compositions HCN,H_2O and $HCN,2H_2O$* respectively, from which it was erroneously inferred that compounds having these formulæ existed. Lespieau (*Compt. rend.*, 1905, **140**, 855) determined the freezing points of solutions of water in hydrogen cyanide up to a concentration of 6·8 g. of water in 100 g. of hydrogen cyanide. In view of the scanty data available, we have therefore studied the solid–liquid equilibria of the system.

EXPERIMENTAL.

The hydrogen cyanide was prepared by the method used by Coates, Hinkel, and Angel (J., 1928, 540), and was distilled from phosphoric oxide, this operation being repeated once or twice with a fractionating column in the case of those samples used for the determination of the f. p. of pure hydrogen cyanide. Conductivity water from a Hartley still was employed. Fig. 1 shows the apparatus used to investigate the stable equilibria of the system. The freezing-point vessel A, 14 cm. long and 3 cm. wide, was fitted with a mercury thermometer B reading from 30° to $-30°$ in 0·1°, the lowest mark being just above the level of the cork C. Stirring was provided by the magnetic stirrer D (behind the thermometer in the figure), operated by the coil E and a motor-driven make-and-break. The cork C, firmly wired down and sealed with paraffin wax, which is inert to and insoluble in hydrogen cyanide, was extended by a wax cylinder F which served to reduce the vapour space. To prepare a

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* All Gautier's mixtures contained the components in simple molecular proportions.

mixture, the taps J, K, L, and M were set so as to allow water to run from the reservoir G, and hydrogen cyanide to be forced from H by the rubber bulb N into A, the relative amounts being roughly estimated by graduations on the latter. The total volume of the mixture was usually 20—30 c.c. In order to be sure that any liquid left in the tube leading from the reservoirs had the same composition as the mixture to be frozen, the latter was passed to and fro along the tube by operating the bulbs O and P after suitably setting the taps K and M. Any overflow from this operation was caught in the trap Q. The taps L and M were then turned off and the mixture was ready to be frozen. The cooling bath R contained liquid sulphur dioxide which could be evaporated at any desired rate by means of a filter pump. There was a narrow air-space between A and the inner wall of R. By means of the pentane thermometer S, the temperature head could be observed and was regulated by the filter pump so as to give a rate of cooling of 0·25—0·5° per minute in the neighbourhood of the f. p.

FIG. 1.

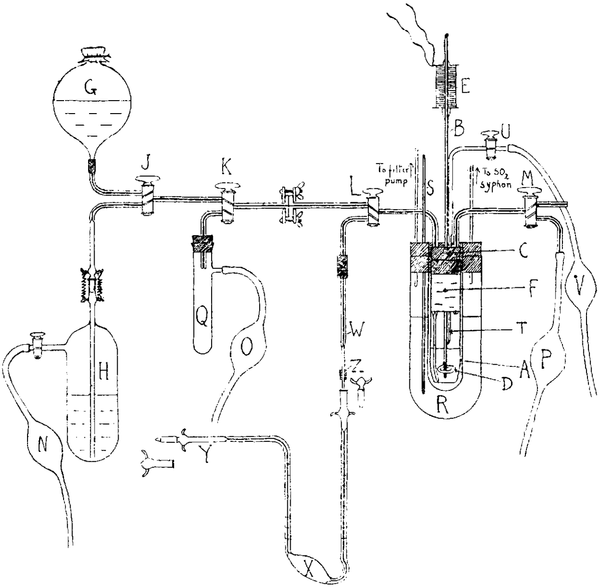
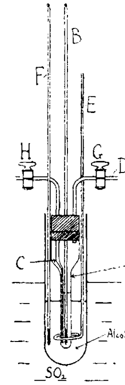


FIG. 2.



The f. p.'s of the mixtures were determined by the back extrapolation of time–temperature curves over the supercooling region. This method is not free from objection, especially if the degree of supercooling is large and, as is the case with mixtures near the eutectic point, the rate of temperature drop is rapid. However, for mixtures not too near the eutectic point, the temperature fell so slowly after crystallisation had started that extrapolation gave results generally trustworthy to 0·1°. In many cases the f. p. was confirmed by heating-curve experiments. With mixtures near the eutectic, however, the temperature drop was so rapid that even with a moderate degree of supercooling, extrapolation gave extremely uncertain results. We were able to remedy this completely by reducing the degree of supercooling to the order of 0·5° or less by means of the device lettered T in Fig. 1. This consisted of a tube drawn to a very fine jet and bent so that, by opening the taps U and M and operating the bulb V, a stream of air could be directed at the stem of the stirrer a short distance above the level of the liquid. The rapid evaporation and consequent cooling of the liquid on the stem on its upward stroke caused crystals to form which inoculated the mixture on the downward stroke. Immediately crystallisation had started, the taps U and M were closed, and since the jet of T was extremely fine, the loss of vapour during the whole operation was negligible.

A portion of the mixture was then removed for analysis by putting W and A into communication and, by means of bulb P, first washing out tube W, and then filling the pyknometer X which was attached to W by the cork Z. The pyknometer with graduated limbs served to measure the densities, which, however, are not reported here, except in the case of pure hydrogen cyanide, as they have now been determined in a more accurate form of pyknometer (Coates and Collins, unpublished work). The two sets of determinations agree within the limits of accuracy imposed by the apparatus. The present determinations served a useful purpose by fixing the compositions of a few mixtures the analyses of which were uncertain.

After the pyknometer had been weighed, the end Y was dipped into a solution containing an excess of sodium hydroxide, and the other end was attached to a reservoir of distilled water, all these operations being carried out as expeditiously as possible. The mixture was thus washed out into the sodium hydroxide solution. The sodium cyanide in the resulting solution was then titrated with silver nitrate solution (Liebig's method). This titration gives excellent results with silver nitrate not stronger than $N/10$. The more concentrated silver nitrate necessary to titrate the whole of the contents of the pyknometer in the case of all mixtures but those weak in hydrogen cyanide gave a curdy precipitate not readily soluble in the excess of sodium cyanide. This difficulty was overcome in two ways : (1) The titration was commenced with concentrated silver nitrate, the cyanide solution being in a bottle which could be stoppered and vigorously shaken, thus dissolving the precipitate fairly easily; when the end-point was nearly reached, the titration was completed with $N/10$-silver nitrate. (2) The cyanide solution was made up to standard volume and an aliquot portion removed by a pipette which passed through a rubber stopper carrying also a rubber pressure bulb and fixed in the neck of the standard flask. The pipette could thus be filled by operating the bulb, and all danger avoided. Of these two ways, the latter, although perhaps not so accurate, proved to be the more convenient, and also had the advantages that several titrations of the same mixture could be made, and that much less silver nitrate was required.

All those parts of the apparatus in contact with the mixtures or their vapour, with the exception of the thermometer, were made of Pyrex glass well steamed before use. The thermometer was treated by standing it in distilled water for a week. A tap lubricant consisting of equal parts of paraffin wax and medicinal paraffin was found to be suitable. By the exercise of these precautions, polymerisation of the hydrogen cyanide was of very infrequent occurrence, though it could not be entirely prevented. The freezing points here recorded refer to mixtures which were entirely colourless.

The results in the metastable region were obtained by means of the apparatus shown in Fig. 2, in the design of which the following points had to be considered : (1) stirring was inadmissible, since it would probably have led to early crystallisation of the stable phase; (2) a fairly rapid rate of cooling was desirable, since the longer a solution remains supersaturated the more likely is it to crystallise; (3) the temperature gradient between the cooling bath and the solution had to be small, and the temperature of the latter as uniform as possible, if the temperature of any event occurring in it were to be recorded with any approach to accuracy. The apparatus in Fig. 2 represents a compromise between these somewhat conflicting requirements. The narrow thin-walled vessel A (made from an ordinary test-tube sealed to a wider tube at the top), containing 5—10 c.c. of the mixture, was provided with a waxed cork carrying a thermometer B * graduated from 30° to —30° in 0·1°, and a tube C through which a sample of the mixture could be collected in the pyknometer previously described by operating a bulb attached to tube D, after opening the taps G and H. A was placed in the inner compartment of a sulphur dioxide bath, as shown in the figure, this compartment being filled with alcohol to a level of 0·5—1 cm. below that of the mixture in A. The object of this was to prevent freezing at the surface of the mixture, since it had fre-

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* Owing to breakage of the thermometer used for the stable region, a new one was used (see paragraph at end of this section).

quently been observed that a film of solid readily forms on the walls above the liquid and so is likely to inoculate it. The alcohol was stirred by means of the hand stirrer E, and its temperature was observed by the thermometer F which was of the same quality and was graduated similarly to B. To carry out an experiment, the rate of cooling was regulated so that with fairly rapid manipulation of E, the temperature difference between the two thermometers was not more than 1°. The mean of these two temperatures was taken as that of any event in A, except in the few cases where the metastable crystals persisted so long that the thermometer B started to rise, in which case the temperature taken was that recorded by this one alone. A very large number of experiments had to be made to obtain even the few results now recorded, since a large proportion of them failed to reach the required degree of supercooling. It was found that, in general, the supercooling could be increased by coating the inside of A and its contents with a thin film of paraffin wax. This was done by filling the apparatus with a solution of wax in pure benzene, which was then poured out, and the benzene in the solution left on the walls allowed to evaporate. The resulting film was so thin that it did not interfere with visibility in the slightest.

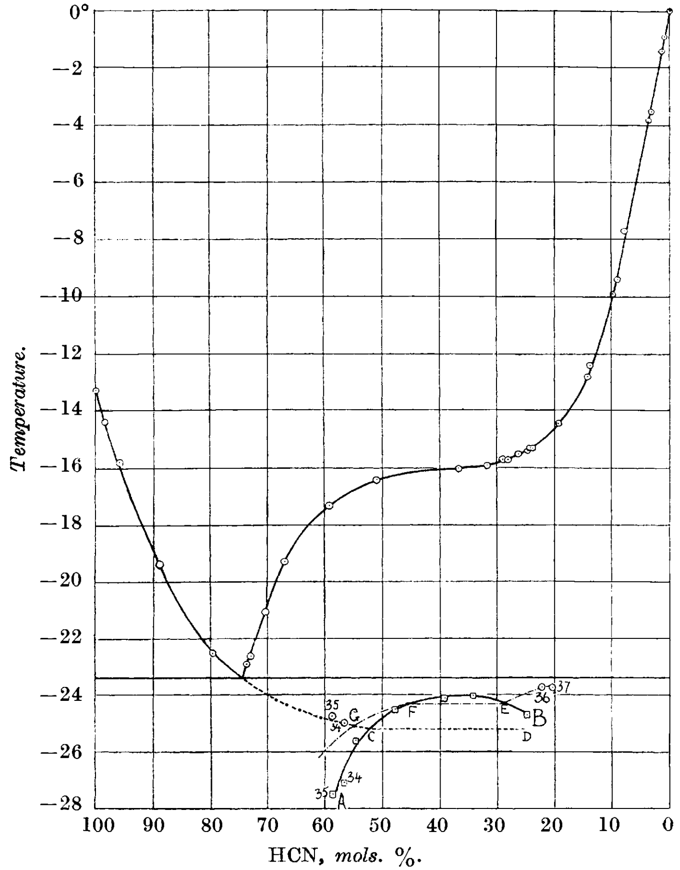
The thermometers used in this work were of " standard " grade, specially made by Messrs. Calderara. Thermometer B (Fig. 1) was in agreement with thermometer B (Fig. 2) at 0° and —23° to within 0·05°, and the latter and thermometer F (Fig. 2) were in agreement with a standard at 0° and at —18° to within 0·05°. Since f. p.'s determined by this method are not precision data, a more complete standardisation was not considered necessary.

Results.

The results are given in Tables I (stable region) and II (metastable region), and are plotted in Fig. 3. The temperatures recorded in these tables have been corrected for the emergence of the thermometer stem, the correction being near —0·2° in all cases. The f. p. found for pure hydrogen cyanide was —13·3°, and its density ($D_{18^\circ}^{18^\circ}$, uncorrected for buoyancy) was 0·6906, which is identical with the value found under the same conditions by Coates and Collins (*vide supra*).

The system is of the simple eutectic type, the co-ordinates of the eutectic point being —23·4° (mean value of all accurately observed arrest temperatures) and 74·5 mols.% of hydrogen cyanide. On the water side of the diagram (Fig. 3) the f. p. curve is linear up to 9·1 mols.% of hydrogen cyanide and corresponds to a normal molecular weight for the latter within 2%. On the hydrogen cyanide side a normal molecular weight for water within 2% is given by the f. p. of a solution containing 99 mols.% of hydrogen cyanide (the value 1942 cals./mol. being used for the latent heat of fusion of hydrogen cyanide, as found by Sinozaki, Hara, and Mitsukuri, *Tech. Rep. Tohoku Imp. Univ.*, 1927, **4**, 157). At higher concentrations of water the solutions rapidly diverge from ideality. These results agree well with those of Lespieau (*loc. cit.*).

FIG. 3.



The water branch of the freezing-point curve shows a marked inflexion at about 35 mols.% of hydrogen cyanide and −16·0°. This inflexion suggested the proximity of a metastable region of two liquid phases, which was actually found on supercooling in the apparatus already described. The results are given in Table II and are plotted as the continuous curve AB in Fig. 3. This curve

TABLE I.

Stable equilibria.

Mixture No.	F. p.	Eutectic arrest.	HCN, mols. %.	Mixture No.	F. p.	Eutectic arrest.	HCN, mols. %.
1	−0·9°	—	0·81	17	−15·9°	−23·40°	31·76
2	−1·4	—	1·27	18	−16·0	−23·43	36·82
3	−3·5	−23·31°	3·09	19	−16·4	−23·34	50·96
4	−3·8	—	3·53	20	−17·3	−23·34	59·24
5	−7·7	—	7·76	21	−19·3	−23·36	66·96
6	−9·4	−23·43	9·03	22	−21·1	−23·44	70·4
7	−9·9	—	9·89	23	−22·6	−23·36	73·0
8	−12·4	—	13·87	24	−22·9	−23·39	73·7
9	−12·8	−23·41	14·25	25	−22·5	−23·45	79·7
10	−14·45	—	19·36	26	−19·4	−23·4	88·9
11	−15·3	−23·40	23·87	27	−15·8	between −23·5 and −25·0	95·9
12	−15·3	—	24·11				
13	−15·4	−23·41	24·61	28	−14·4	between −24·5 and −26·0	98·5
14	−15·5	−23·43	26·29				
15	−15·7	−23·41	28·03	Pure HCN	−13·3		
16	−15·7	—	28·99				

Mean value −23·4°

TABLE II.

Metastable equilibria.

Mixture No.	Mean temperature at which two liquid phases appeared.	HCN, mols. %.
29	−24·7°	24·8
30	−24·0	34·4
31	−24·1	39·2
32	−24·5	47·9
33	−25·6	54·7
34	−27·1	56·7
35	−27·5	58·7

shows the critical solution temperature to be near −24·0°, the critical composition corresponding almost exactly with that of the inflexion on the f. p. curve, *viz.*, 35 mols.%.

In addition to the separation into two liquid phases, the supercooled solutions frequently deposited metastable crystals which we were usually able to classify as being either (*a*) dendritic and rapid-growing, or (*b*) compact and slow-growing. The temperatures at which they appeared corresponded, of course, to different and fortuitous degrees of supercooling and were therefore of no use for finding the metastable f. p.'s. Only in a few cases did a sufficient quantity of the crystals form for the inner thermometer to rise and enable an estimate of the f. p. to be made; usually the crystallisation of ice and the consequent disappearance of all metastable phases occurred too soon. The following evidence obtained from these few cases, however, indicated the existence of two metastable solids, in agreement with the above classification of the crystals into two kinds according to their appearance and rate of growth. Mixture 34, soon after separating into two liquid phases (point 34, line AB, Fig. 3), deposited the rapid-growing dendritic crystals, whereupon the inner thermometer rose to —25·2°, remained there for about a minute, and then rose slowly to —25·0°, after which crystallisation of ice supervened. The arrest at —25·2° is assumed to have been due to the presence of two liquid phases as well as the solid, the subsequent rise to —25·0° signalising the disappearance of one of the liquid phases. These observations agree with the solid being metastable hydrogen cyanide, for, as Fig. 3 shows, extrapolation of the hydrogen cyanide branch of the f. p. curve can be carried out quite smoothly to cut AB at —25·2° (point C). The highest point reached by the mixture, *viz.*, —25·0°, also lies on the extrapolated curve, although it is not, of course, certain that the temperature would not have risen further if the ice had crystallised later. The slowness of the rise, however, indicated that it was near, if not actually at, its maximum when this happened.

Mixtures 36 and 37 (Fig. 3, not included in Table II), containing 22·2 and 20·4 mols.% of hydrogen cyanide respectively, did not separate into two liquids but deposited crystals which in the case of No. 36 were of the compact slow-growing variety. (Our experimental notes do not record the appearance of the crystals of Mixture 37, because it had not then been realised that there were two solids in question, but judging from the similarity in the behaviour of the two mixtures it seems justifiable to conclude that the same solid was concerned in both cases.) The crystals in both mixtures grew for a considerable period and the inner thermometer rose to —23·7° on both occasions before ice separated. The temperature had become almost stationary before this happened, so that —23·7° was probably very near, if not actually the value of the f. p.'s of the mixtures. If the solid separating from these mixtures had been metastable hydrogen cyanide, the f. p.'s would have been lower, not higher, than the temperature of the triple point line CD. We therefore assume that it was a different substance, and if we exclude a metastable form of ice, the only possibility is that it was a metastable compound of hydrogen cyanide and water, probably richer in water than Mixture 36. A possible relationship of the f. p. curve of this solid with the other metastable phases is suggested by the lines EF and FG, although the curve may pass above the critical solution temperature instead of below it. In either case the substance seems to form a eutectic with metastable hydrogen cyanide at a point not far removed from G, because Mixture 35, after separating into two liquids (point 35, line AB, Fig. 3), deposited first the compact crystals and then the dendritic crystals, apparently with decomposition of the former kind, indicating that they were unstable.

The whole process was accompanied by a rise of temperature which included a short arrest at —25·2° and a slow finish at —24·7°, which lies very close to the extrapolated hydrogen cyanide curve at this composition.

In view of the extreme difficulty of obtaining an adequate number of reasonably precise data for f. p.'s in the metastable region, the above observations regarding the metastable solid–liquid system must be considered as tentative only.

The limited miscibility of hydrogen cyanide and water at low temperatures may be correlated with the large positive deviation of this system from ideality as shown by the partial vapour-pressure measurements of Shirado (*Bull. Chem. Soc. Japan*, 1927, **2**, 85). Further, whilst propionitrile and water exhibit partial miscibility with a critical solution temperature of 113·1° (Rothmund, *Z. physikal. Chem.*, 1898, **26**, 433), acetonitrile and water have a critical solution temperature in the region of 0° (private communication; the system is under investigation in this laboratory). Thus the system hydrogen cyanide and water fits into the nitrile series as regards this property.

Summary.

1. The solid–liquid equilibria in the system hydrogen cyanide and water have been studied. The stable f. p. curve is of the simple eutectic type, the co-ordinates of the eutectic point being —23·4° and 74·5 mols.% of hydrogen cyanide. The water branch is ideal up to 9·1 mols.% of hydrogen cyanide, and the other branch up to 1 mol.% of water.

2. The water branch has a marked inflexion at about 35 mols.% of hydrogen cyanide and —16·0°. The metastable two-liquid phase region to be expected from this inflexion has been found, the critical solution temperature being near —24·0°.

3. Two types of metastable solid phase have been recognised, one of which is thought to be hydrogen cyanide, and the other a compound of hydrogen cyanide and water.

4. The limited miscibility of hydrogen cyanide and water agrees with the large positive deviation from ideality shown by partial vapour-pressure measurements. The critical solution temperature is lower than that of acetonitrile and water, which in turn is lower than that of propionitrile and water.

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University College of Swansea,
University of Wales.

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