Redox Extractions from Molten Alkali-metal Cyanides. Part 2.[1] Mechanism for Extractions with Liquid Tin Alloys

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Cyanide is the reductant during the extraction of metal ions from molten cyanide solutions with liquid tin alloys. Infrared studies revealed that molten cyanide is oxidised to dicyanamide, and that the redox potential of a cyanide melt is determined by the dicyanamide $\rightleftharpoons$ cyanamide equilibrium; the latter is the reduction product of dicyanamide.

In Part 1[1] the extraction of metal ions from molten cyanide solution into zinc-containing alloys was interpreted in terms of the exchange equilibrium (A). Extractions from molten cyanide can also be carried out with tin, bismuth, lead, or alloys of these elements, and, since the oxidised forms of these elements are unstable in molten cyanide, exchange-type mechanisms seem unlikely for such extractions.

$$\underset{\text{salt}}{M^{m+}} + \underset{\text{metal}}{\frac{m}{2}\,Zn} \rightleftharpoons \underset{\text{metal}}{M} + \underset{\text{salt}}{\frac{m}{2}\,Zn^{2+}} \qquad \text{(A)}$$

In this paper a general relation between the distribution of a solute and the composition of the system is derived from electrochemical principles. This relation is shown to fit experimental data obtained both with alloys containing zinc and alloys without zinc. The extraction mechanism for tin-containing metal phases that follows from this relation is then verified by i.r. studies on quenched cyanide melts.

EXPERIMENTAL

Reagents and Solutions.—Salt phases (eutectic NaCN–KCN containing 53% by weight of NaCN) were purified from carbonate by the filtration technique described elsewhere.[2] Sodium dicyanamide and disodium cyanamide (Eastman Kodak 'Practical grade' reagents) were used as purchased, except for drying under vacuum (1.2 Pa). Molten cyanide solutions of these reagents were prepared by adding weighed amounts to the salt prior to filtration. To prevent excessive polymerisation, dicyanamide was, in some experiments, dissolved in the filtered melt immediately before an experiment was started.

Metal-ion solutions were prepared by adding weighed amounts of the metal chlorides to the salt before filtration. These metals were assumed to be present in solution as cyanide complexes only.

I.r. Spectra.—Spectra in the 1 900—625 cm^{-1} range were obtained as described before,[2] and those in the 2 500—1 900 cm^{-1} range by the method of de Haas *et al.*[3a] Samples from molten solutions were obtained by removing the layer of quenched salt from a glass rod which was dipped into the melt. Peaks are numbered in the Figures, and the origin and wavelength corresponding to a peak can be obtained from Table 1. Molten cyanide was oxidised by adding anhydrous stannous chloride (2 g) to the melt (15 g).

Oxidations with Dicyanamide.—The quantitative oxidising ability of dicyanamide was determined from the amount of copper or zinc dissolved by a 4% dicyanamide solution in molten cyanide. The amount dissolved was determined from the loss of weight. Because of the lack of a suitable

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[1] Part 1, J. G. V. Lessing, K. F. Fouché, and T. T. Retief, preceding paper.

[2] J. G. V. Lessing, K. F. Fouché, and T. T. Retief, *Electrochim. Acta*, 1977, **22**, 391.

[3] (*a*) K. S. de Haas, K. F. Fouché, and C. M. Fouché, *Inorg. Chim. Acta*, 1977, **21**, 15; (*b*) K. S. de Haas and K. F. Fouché, *Inorg. Chim. Acta*, 1977, **24**, 267.

analytical method, the unchanged dicyanamide was not determined.

Extractions.—Extractions were performed as described in Part 1.[1] All experiments with molten cyanide were carried out at 530 ± 3 °C.

TABLE 1

Origin and wavenumber of the numbered peaks appearing in Figures 3—10

No.	Compound	ν/cm^{-1}	No.	Compound	ν/cm^{-1}
1	CNO^-	630 [a]	20	$[\{N(CN)_2\}_3]^{3-}$	1 410 [d]
2	$[N(CN)_2]^-$	664 [b] 670 [d]	21	$[CO_3]^{2-}$	1 435 [a]
3	$[CO_3]^{2-}$	705 [a]	22	$[\{N(CN)_2\}_3]^{3-}$	1 490 [d]
4	$[(HNCN)_3]^{3-}$	765 [d]	23	$[(HNCN)_3]^{3-}$	1 550 [d]
5	$[(NCN)_3]^{6-}$	800 [d]	24	$[\{N(CN)_2\}_3]^{3-}$	1 595 [d]
6	$[(N(CN)_2)_3]^{3-}$	810 [d]	25	$[CO_3]^{2-}$	1 700 [a]
7	$[(HNCN)_3]^{3-}$	812 [d]	26	$[Ni(CN)_4]^{4-}$	1 967 [c]
8	$[CO_3]^{2-}$	885 [a]	27	$[(NCN)_3]^{6-}$	1 970 [d]
9	$[N(CN)_2]^-$	930 [b] 933 [d]	28	$[Ni_2(CN)_6]^{4-}$	2 045 [c]
10	$[(NCN)_3]^{6-}$	1 000 [d]	29	$[Rh(CN)_4]^{3-}$	2 048 [c]
11	$[\{N(CN)_2\}_3]^{3-}$	1 025 [d]	30	(K,Na)CN	2 058 [c]
12	$[(HNCN)_3]^{3-}$	1 160 [d]	31	$[Pd(CN)_4]^{2-}$	2 120 [c]
13	$[(HNCN)_3]^{3-}$	1 197 [d]	32	$[Ni(CN)_4]^{2-}$	2 125 [c]
14	CNO^-	1 210 [d]	33	$[Rh(CN)_6]^{3-}$	2 130 [c]
15	$[(HNCN)_3]^{3-}$	1 240 [d]	34	$[\{N(CN)_2\}_3]^{3-}$	2 180 [d]
16	$[\{N(CN)_2\}_3]^{3-}$	1 242 [d]	34	$[N(CN)_2]^-$	2 180 [b]
17	CNO^-	1 300 [a]	35	$[N(CN)_2]^-$	2 230 [b]
18	$[N(CN)_2]^-$	1 344 [b] 1 335 [d]	36	$[N(CN)_2]^-$	2 287 [b]
19	$[(NCN)_3]^{6-}$	1 350 [d] 1 344 [d]			

[a] R. A. Nyquist and R. O. Kagel, 'Infrared Spectra of Inorganic Compounds (3 800—45 cm^{-1}),' Academic Press, New York, 1971. [b] Ref. 8. [c] Ref. 3. [d] This work.

RESULTS AND DISCUSSION

Equilibrium in Molten Salt–Liquid Metal Systems.—Chemical equilibrium in a liquid metal–molten salt system implies that the Nernst potential of the alloy and redox potential of the melt are equal. This equality can, in principle, be experimentally verified by measuring the e.m.f. between an inert electrode in the salt and the liquid alloy. Any deviation of this value from zero will act as a driving force for the oxidation of the alloy by the melt. This reaction will lower the oxidation potential of the melt, increase the Nernst potential of the alloy, and stop when the two potentials are equal. If such a reaction is not possible or can be considered negligible the alloy is regarded as inert in the melt.

The redox potential E of the system can be quantified by measuring the e.m.f. between the alloy (or inert electrode) and a suitable reference electrode. The equilibrium value of E characterises a unique distribution of the components between the two phases, and, as is shown below, can be used to determine the distribution of any single component.

At equilibrium the Nernst potentials of all metal–metal salt couples in the system are equal to E. Thus for a metal M we have (1). Here $e_{\mathrm{M}}^{\ominus}$ is the standard reduction potential of M, m is the oxidation state of M in the salt, and a denotes activities. The distribution coefficient of M was defined as [1] in relation (2), where x designates mole or atom fractions, and $a = \gamma x$, $\gamma \rightarrow 1$ if $x \rightarrow 1$.

$$E = e_{\mathrm{M}}^{\ominus} + \frac{\boldsymbol{RT}}{mF}\ln\left(\frac{a_{\mathrm{M}^{m+}}}{a_{\mathrm{M}}}\right) \qquad (1)$$

$$q = \frac{x_{\mathrm{M}}}{x_{\mathrm{M}^{m+}}} \qquad (2)$$

From equations (1) and (2) we obtain (3). This then is

$$\log q = \frac{-mF}{2.3\boldsymbol{RT}}\,(E - e_{\mathrm{M}}^{\ominus}) + \log \gamma_{\mathrm{M}^{m+}} - \log \gamma_{\mathrm{M}} \qquad (3)$$

the general relation between the distribution coefficient of a solute M and the composition of the extraction system. To obtain a useful relationship, the same simplification as in Part 1 can be applied, *i.e.* the distribution of a minute quantity of M is to be considered. The composition of the salt phase can then be assumed constant, and q can be determined as a function of the composition of the metal phase (*i.e.* x_{R}) only. Furthermore, γ_{M} can then be calculated from the approximation used by Johnson[4] to calculate the activity coefficient of a dilute solute (M) in a binary alloy (R,S). Here

$$\log \gamma_{\mathrm{M}} = x_{\mathrm{R}} \log (\gamma_{\mathrm{M}})_{\mathrm{R}} + x_{\mathrm{S}} \log (\gamma_{\mathrm{M}})_{\mathrm{S}} \qquad (4)$$

$(\gamma_{\mathrm{M}})_{\mathrm{R}}$ and $(\gamma_{\mathrm{M}})_{\mathrm{S}}$ are the activity coefficients of M at infinite dilution in pure R and S respectively. It then follows from (3), (4) and the relation $x_{\mathrm{S}} = 1 - x_{\mathrm{R}}$ that

$$\log q = \text{constant} - \frac{mFE}{2.3\boldsymbol{RT}} - \beta x_{\mathrm{R}} \qquad (5)$$

where

$$\beta = \log (\gamma_{\mathrm{M}})_{\mathrm{R}} - \log (\gamma_{\mathrm{M}})_{\mathrm{S}} \qquad (6)$$

For extraction systems such as the Zn–$Zn(CN)_2$ system discussed in Part 1, E can be calculated from the Nernst potential of the reductant (*i.e.* zinc) as in (7). By

$$E = e_{\mathrm{Zn}}^{\ominus} + \frac{2.3\boldsymbol{RT}}{2F}\log\left[\frac{a_{\mathrm{Zn(CN)_2}}}{a_{\mathrm{Zn}}}\right] \qquad (7)$$

substituting (7) into (5) and maintaining the condition of constant salt-phase composition, the relation can be obtained. In Part 1 this equation was shown to originate from an exchange mechanism.

$$\log q = \text{constant} + \frac{m}{2}\log a_{\mathrm{Zn}} - \beta x_{\mathrm{Zn}} \qquad (8)$$

Since oxidised forms of metals such as Bi, Sn, and Pb were never detected in molten cyanide, these metals can be regarded as inert in molten cyanide and they will thus reflect the redox potential of the melt.

The redox potential of a system composed of one or more of these metals and a molten cyanide phase will thus be equal to the oxidation potential of the melt and will, therefore, be determined by the composition of the

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[4] I. Johnson, in 'Application of Fundamental Thermodynamics to Metallurgical Processes,' ed. G. R. Fritterer, Gordon and Breach, New York, 1967, p. 154.

salt phase only. If the latter is kept constant, E will be constant, and equation (5) is reduced to (9). Equation

$$\log q = \text{constant} - \beta x_{\mathrm{R}} \qquad (9)$$
$$(\mathrm{R} = \mathrm{Sn, Pb, or Bi})$$

(9) indicates that if (4) is valid, $\log q$ is a linear function of the composition of an inert alloy.

It is significant to note that equation (9) was derived without reference being made as to how electroneutrality in the extraction system is maintained. This matter will be further discussed after comparison of (9) with experimental results.

Equilibrium in the (K,Na)CN/Bi–Sn *System*.—In order to obtain experimental data suitable for testing equation (9), it would be necessary to do extractions in such a way that the value of E is reproducible. Analysis of the factors determining E revealed that this is hardly possible, except in systems where a substantial amount of the oxidised form of the reductant is added to the salt phase so that E is determined by the Nernst potential of the reductant.

The oxidation potential of a binary melt is determined by the equilibrium position in the dissociation reaction of the least-stable component; *i.e.* for a KCN–NaCN melt where E can be calculated from either (11) or (12). As a

$$\mathrm{NaCN} \rightleftharpoons \mathrm{Na} + \tfrac{1}{2}(\mathrm{CN})_2 \qquad (10)$$

$$E = e_{\mathrm{Na}}^{\ominus} + \frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln\left[\frac{a_{\mathrm{Na}^+}}{a_{\mathrm{Na}}}\right] \qquad (11)$$

$$E = e_{(\mathrm{CN})_2}^{\ominus} + \frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln\left[\frac{\{a_{(\mathrm{CN})_2}\}^{\frac{1}{2}}}{a_{\mathrm{CN}^-}}\right] \qquad (12)$$

result of the high stability of alkali metal cyanides, the concentration of dissociation products (both soluble in the melt) will be very low. The value of E [equations (11) and (12)] is thus easily affected by *e.g.* reaction of Na or $(\mathrm{CN})_2$ with impurities, volatalisation, adsorption on containers, *etc.*

It was experimentally found that although it usually took >5 h for E to stabilise, it thereafter remained constant for several hours. This is reflected by the results in Figure 1 where the extraction of iridium tracer from (K,Na)CN into a Bi–Sn alloy is shown for several different experiments. A constant but not reproducible E will result in a series of parallel extraction curves [equation (9) where the value of the constant is changed by E]. This seems to be the case in Figure 1. The value of $-\beta$ can be calculated from the slope of these lines. A theoretical value for β cannot be calculated, since no thermodynamic data are available.[5] It can, however, be compared with the value to be expected from the results in Part 1,[1] since relation (13) follows from (6),

$$(\beta_{\mathrm{Ir}})_{\mathrm{Bi\text{-}Sn}} = (\beta_{\mathrm{Ir}})_{\mathrm{Bi\text{-}Zn}} - (\beta_{\mathrm{Ir}})_{\mathrm{Sn\text{-}Zn}} \qquad (13)$$

where $(\beta_{\mathrm{Ir}})_{\mathrm{Bi\text{-}Sn}}$, $(\beta_{\mathrm{Ir}})_{\mathrm{Bi\text{-}Zn}}$, and $(\beta_{\mathrm{Ir}})_{\mathrm{Sn\text{-}Zn}}$ are the slopes of the extraction curves in the three respective systems. The β values on the right of equation (13) were experimentally determined in Part 1. The value of $(\beta_{\mathrm{Ir}})_{\mathrm{Bi\text{-}Sn}}$ calculated from this data and equation (13) (5.90 ± 1.20) compares favourably with the average slope of the lines in Figure 1 (6.13 ± 1.11).

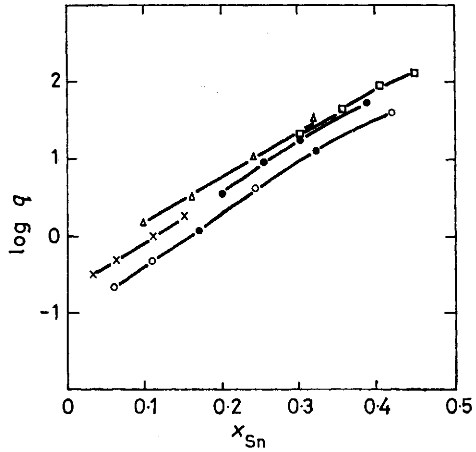

FIGURE 1 Distribution of iridium tracer in the system (K,Na)CN/Bi–Sn obtained from various experiments. Results indicated by ● on the lowest curve were obtained during a back-extraction, and prove the reversibility of the results within any single experiment

Extraction results for copper are shown in Figure 2.

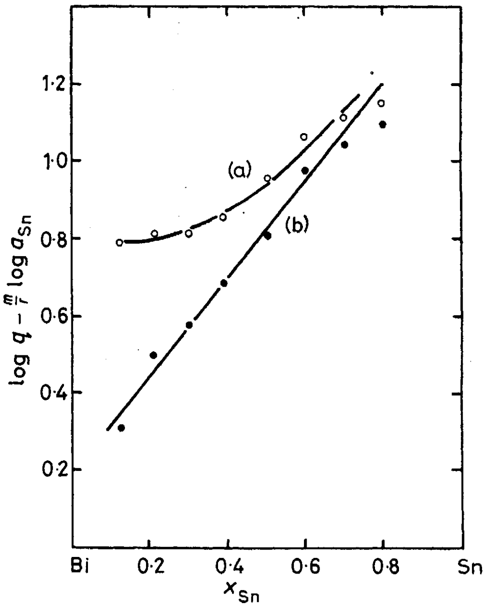

FIGURE 2 Distribution of copper tracer in the system (K,Na)CN/Bi–Sn. Results are plotted for (a) tin as reductant ($m/r = \frac{1}{2}$) and (b) cyanide as reductant ($m/r = 0$)

These results are plotted according to (*a*) equation (8) (exchange mechanism) and (*b*) equation (9). In applying equation (8) (with a_{Zn} and x_{Zn} replaced by a_{Sn} and x_{Sn}, respectively) to the results, an oxidation state of +2 was

[5] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, 'Selected Values of Thermodynamic Properties of Metals and Alloys,' John Wiley and Sons, New York, 1963.

assumed for tin in the melt, and in determining F (see Part 1 [1]) $x_{\mathrm{Sn(CN)_2}}$ was taken as zero. The simpler linear relationship is obtained by applying equation (9) only. The slope of this line (1.21 ± 0.11) compares favourably with the value (1.34 ± 0.14) calculated from equation (6) and the results found in Part 1.[1]

Straight lines were obtained for both equations (8) and (9) when the results for iridium are plotted. This is due to the fact that $-\frac{1}{2}\log a_{\mathrm{Sn}}$ can be considered a linear function of x_{Sn} for $0.2 \leqslant x_{\mathrm{Sn}} \leqslant 0.3$. The slope of the line resulting from equation (9) (6.13 ± 1.11) is, however, closer to the calculated value (5.90) than that resulting from equation (8) (5.34 ± 1.11).

It can thus be concluded that the experimental data are in support of an extraction mechanism where tin (thus probably also bismuth and lead) acts only as a solvent and not as an electron donor. The latter seems to be cyanide.

Molten Cyanide as Reductant.—The reduction of metal ions to lower oxidation states when dissolved in molten cyanide was reported to result in the oxidation of cyanide to cyanogen.[6,7] A possible extraction mechanism with cyanide as reductant is then (14). The spontaneous extraction of M^{m+} is thus caused by the formation of the M–Sn intermetallic compound.

$$\underset{\text{salt}}{M^{m+}} + \underset{\text{salt}}{m\mathrm{CN}^-} + \underset{\text{metal}}{x\mathrm{Sn}} \rightleftharpoons \underset{\text{metal}}{\mathrm{MSn}_x} + \underset{\text{salt}}{\frac{m}{2}(\mathrm{CN})_2} \qquad (14)$$

Franklin [8] pointed out that in 1871 Bannow reported the use of the reaction between cyanogen and molten cyanide for the synthesis of dicyanamide. It can,

$$(\mathrm{CN})_2 + \mathrm{CN}^- \longrightarrow [\mathrm{N(CN)_2}]^- + \mathrm{C} \qquad (15)$$

therefore, be expected that the oxidation of molten cyanide will result in the formation of dicyanamide. This was indeed found to be the case, as is proved by the results in Figure 3 where an i.r. spectrum of a cyanide melt oxidised with stannous chloride (which is reduced to tin metal), is shown. The peaks numbered 9, 18, 34, 35, and 36, indicate the presence of dicyanamide,[9] and, as will be shown below, those numbered 6, 20, 22, and 24 can be ascribed to a trimer of dicyanamide.

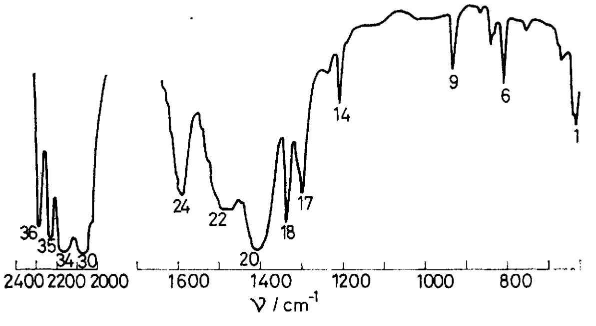

FIGURE 3 I.r. spectrum of a cyanide melt (not purified from carbonate) oxidised with stannous chloride

Equation (15) shows that the extraction of *e.g.* $\mathrm{Pd^{II}}$ with tin should be represented by (16). Physical evidence for this reaction was obtained from (*a*) the appearance of large quantities of a black deposit (not Pd since

$$\mathrm{Pd^{2+}} + 3\,\mathrm{CN}^- + x\mathrm{Sn} \longrightarrow \mathrm{PdSn}_x + [\mathrm{N(CN)_2}]^- + \mathrm{C} \qquad (16)$$

$>95\%$ can be recovered from the metal phase) in the salt phase after $\mathrm{Pd^{II}}$ was extracted from a 4% solution into tin, and (*b*) the presence of dicyanamide in the salt phase after extraction (Figure 4).

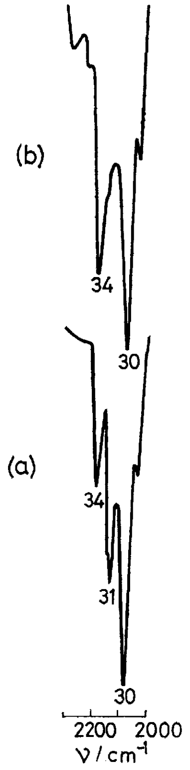

FIGURE 4 I.r. spectrum of a 4% palladium solution in molten cyanide (a) before and (b) after equilibration with 10 g tin. Tetracyanopalladate(II) (peak 31) is reduced to the tin phase while the concentration of dicyanamide (peak 34) is increased

Dicyanamide.—The reversible behaviour of extractions (Figure 1) with tin as metal phase, *i.e.* extractions of the type in reaction (16), indicates that dicyanamide, the oxidation product of cyanide, probably acts as the oxidant in cyanide melts.

The oxidising nature of dicyanamide was qualitatively proved by the lowering of distribution ratios upon addition of dicyanamide (the extraction of *e.g.* Ir decreases from $>90\%$ at $x_{\mathrm{Sn}} = 0.3$ to $<10\%$ upon addition of 0.1% dicyanamide), as well as the dissolution of metals such as Zn, Cu, and Ni by dicyanamide-containing solutions. Figure 5 shows the i.r. spectrum

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[6] S. von Winbush, E. Griswold, and J. Kleinberg, *J. Amer. Chem. Soc.*, 1961, **83**, 3197.

[7] W. L. Magnuson, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, 1964, **3**, 88.

[8] E. C. Franklin, *J. Amer. Chem. Soc.*, 1922, **44**, 486.

[9] M. Kuhn and R. Mecke, *Chem. Ber.*, 1961, **94**, 3010.

of a 4% sodium dicyanamide solution both before and after it was brought into contact with nickel foil. Tetracyanonickelate(II) (peak **32**) is formed while the concentration of dicyanamide (peaks **34**, **35**, and **36**) decreases. Peak **26** at 1 967 cm^{-1} can be attributed to tetracyanonickelate(0) which was shown to form when Ni^{II} is dissolved in a cyanide melt.[6]

The activity of dicyanamide in molten cyanide solution is decreased by polymerisation and reaction with impurities such as carbonate (both effects are discussed later). It can, therefore, be expected that a quantitative determination of the oxidising ability of dicyanamide will give low values. From experiments on the dissolution of copper and zinc in dicyanamide-containing melts, the value for n in the reaction $[N(CN)_2]^- + ne \rightarrow$ products was found to vary from 1.5 and 1.8, depending on the reaction time. An i.r. spectrum of a salt phase showed that dicyanamide was still present (as a trimer) after 5 h. It thus seems that $n \longrightarrow 2$, with (17) as a possible reaction. Thus dicyanamide is reduced to cyanamide.

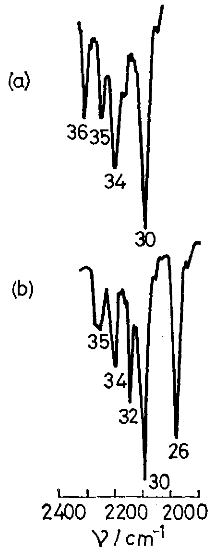

FIGURE 5 I.r. spectrum of a 4% sodium dicyanamide solution in molten cyanide (a) before and (b) after it was reduced with nickel foil. Tetracyanonickelate(II) (peak 32) is formed and partly reduced to tetracyanonickelate(0) (peak 26). The dicyanamide (peaks 34, 35, and 36) concentration is decreased

$$[N(CN)_2]^- + 2\,e \rightleftharpoons NCN^{2-} + CN^- \quad (17)$$

The existence of equilibrium (17) in molten cyanide is proved by the results in Figures 6 and 7. The spectra in Figure 6(*a*) and (*b*) are very similar, and it can be concluded that the same compound is probably present in both samples. The identity of this compound (possibly a polymer of cyanamide) is discussed later.

The reverse of reaction (17), *i.e.* cyanamide oxidised to dicyanamide in molten cyanide solution, is confirmed by the results in Figure 7. Hexacyanorhodate(III) (peak **33**) is reduced to tetracyanorhodate(I) (peak **29**), and cyanamide is oxidised to dicyanamide (peak **34**).

On the basis of the above results it can be concluded

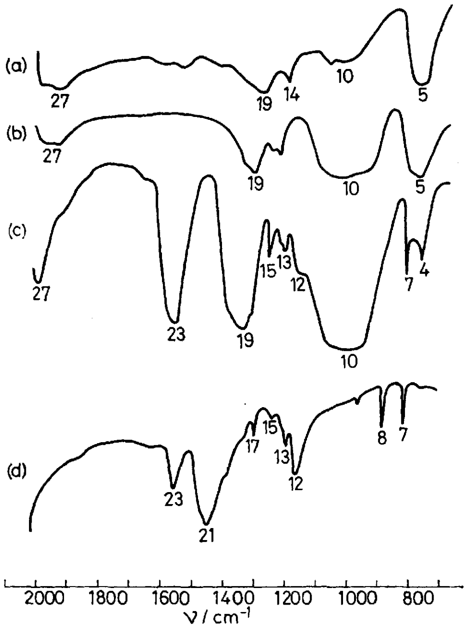

FIGURE 6 I.r. spectra of (a) a 4% sodium dicyanamide solution reduced with copper [compare with Figure 8(d)] and (b) a 10% sodium cyanamide solution in molten cyanide. The spectra (c) and (d) were obtained from the discs used to record spectra (b) and (a) respectively after they were exposed to the atmosphere

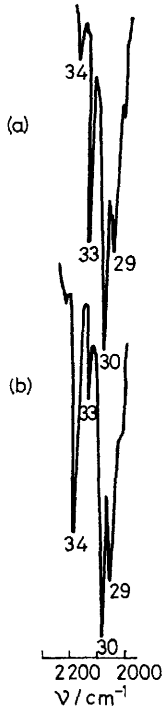

FIGURE 7 I.r. spectrum of a 2.6% Rh^{III} solution (a) before and (b) after the addition of disodium cyanamide (100 mg). Hexacyanorhodate(III) (peak 33) is reduced to tetracyanorhodate(I) (peak 29), and cyanamide is oxidised to dicyanamide (peak 34)

that redox equilibria in cyanide melts are probably controlled by the dicyanamide : cyanamide ratio.

Polymerisation.—Both NCN and $N(CN)_2$ compounds easily condense to *s*-triazine derivatives.[8] The bending mode of the *s*-triazine ring was reported [10] to be near 810 cm^{-1}, and since both cyanamide and dicyanamide solutions have i.r. bands in this region, it seems likely that both reagents polymerise in molten cyanide solution. I.r. spectra for these polymers have not been reported.

A salt of the trimer of dicyanamide can be isolated from a concentrated aqueous solution of sodium dicyanamide,[8] and *X*-ray studies on the structure of this compound revealed that it is indeed a *s*-triazine derivative.[11] In Figure 8 the i.r. spectrum of a salt thus prepared is compared with the spectra of sodium dicyanamide, molten sodium dicyanamide, and a molten cyanide solution of dicyanamide. It is clear that dicyanamide is present in both the monomeric and trimeric forms in molten cyanide solution.

In Figure 9 i.r. spectra of a 4% dicyanamide solution are shown. These spectra were obtained from samples taken after periods of increasing length were allowed for polymerisation. It is evident that after about 3 h the presence of dicyanamide in molten cyanide will, in the range 1 900—2 500 cm^{-1}, be indicated by a single band at 2 180 cm^{-1} (peak 34).

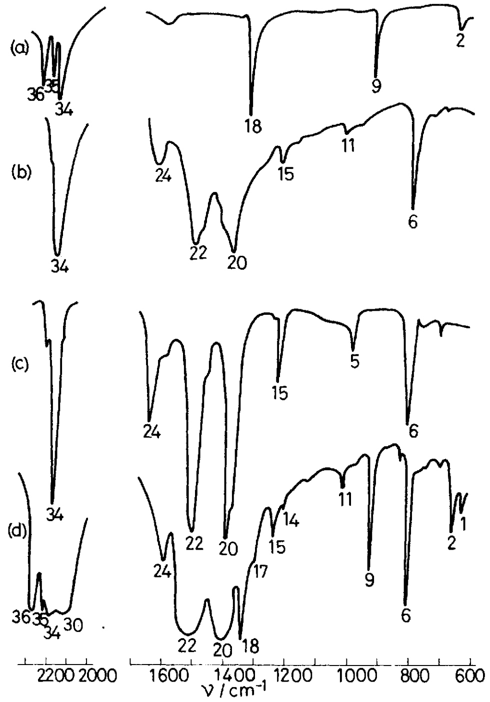

FIGURE 8 I.r. spectra of (a) sodium dicyanamide, (b) molten sodium dicyanamide, (c) trimeric sodium dicyanamide isolated from an aqueous solution, and (d) a 4% solution of sodium dicyanamide in molten cyanide

Comparison of the i.r. spectra of Na_2NCN (Figure 6) in quenched cyanide melts with samples of the salt as prepared from aqueous solutions is of little use, since Sole [12] pointed out that the isolated product is actually the monosodium salt NaHNCN. The changes in i.r. spectra when quenched melts containing Na_2NCN [Figure 6(a) and (b)] are exposed to the atmosphere [Figure 6(c) and (d)] are probably due to hydrolysis

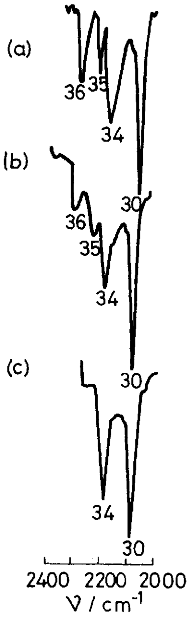

FIGURE 9 I.r. spectrum of a 4% sodium dicyanamide solution (a) 3 min, (b) 2 h, and (c) 5 h after dissolution. The spectrum gradually changes to that of the trimer

$$Na_2NCN + H_2O \longrightarrow NaHNCN + NaOH \quad (18)$$

[equation (18)]. The broad absorption bands and the characteristic *s*-triazine ring peak near 810 cm^{-1} indicate that the spectra in Figure 6(a) and (b) originate from a trimer of Na_2NCN and the spectra in Figure 6(c) and (d) from a trimer of NaHCN.

Impurities.—During this investigation it was also observed that dicyanamide reacts with carbonate to form cyanate. This was evident from several experiments with carbonate-containing melts (prepared from eutectic mixtures which had been vacuum-dried only before melting [2]) which showed that the characteristic i.r. bands of carbonate disappear and those of cyanate appear. It was further verified by adding carbonate to dicyanamide-containing melts and comparing the i.r. spectra. As the redox potential of the melt depends on the activity of dicyanamide, its reaction with carbonate will make the melt more reducing, as was observed during previous investigations.[13]

We thank the Atomic Energy Board for permission to publish these results.

[6/1558 *Received, 9th August*, 1976]

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[10] T. S. Herman, *Appl. Spectroscopy*, 1966, **20**(3), 159.

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