Redox Extractions from Molten Alkali-metal Cyanides. Part 1. Mechanism for Extractions with Liquid Zinc Alloys

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The distribution of Rh, Ir, Ru and Cu between a 9% zinc cyanide solution in molten eutectic KCN–NaCN and a liquid binary alloy of Zn with Bi or Sn was determined at 530 °C. The results fit an exchange-type extraction mechanism *e.g.*

$$\underset{\text{salt phase}}{M(CN)_m} + \underset{\text{metal phase}}{\frac{m}{2}Zn} \rightleftharpoons \underset{\text{metal phase}}{M} + \underset{\text{salt phase}}{\frac{m}{2}Zn(CN)_2}$$

The activity-coefficient ratios of the extracted metal in the components of the binary alloy phases can also be calculated from the distribution data.

THE extraction of a metal ion M^{m+} from a molten salt solution into a liquid metal phase containing a reductant R, is governed by the equilibrium (1).

$$\underset{\text{salt phase}}{M^{m+}} + \underset{\text{metal phase}}{\frac{m}{r}R} \rightleftharpoons \underset{\text{metal phase}}{M} + \underset{\text{salt phase}}{\frac{m}{r}R^{r+}} \qquad (1)$$

This mechanism is valid for extraction systems where the molten salt and liquid metal solvents are inert, *i.e.* redox reactions are limited to M and R only. Previous investigations were generally confined to systems of this kind.

When using molten alkali cyanides as ionic phase, it could be expected that the solvent may also take part in redox reactions since it is known that molten cyanide is highly reducing.[1] Evidence for such behaviour has already been obtained during extractions of the platinum-group metals (Ru, Rh, Pd, Os, Ir, and Pt) from cyanide where it was found that inert (with respect to cyanide) liquid metals such as Bi, Sn, Pb, and In could extract certain platinum-group metals from the melt.[2] Oxidised species of these inert metals could never be detected in the salt phase. Zinc, on the other hand, which forms a stable complex in molten cyanide, was found to be an effective reductant which apparently follows a simple exchange-type mechanism [equation (1)] during extraction.

This paper deals with extractions carried out with liquid zinc alloys, *i.e.* systems where an exchange-type mechanism can be expected. Extractions with liquid metal phases not containing zinc, and the role of cyanide as reductant, are discussed in Part 2.[3]

EXPERIMENTAL

Salt Phase.—Zinc cyanide (10% by mass) was mixed with eutectic KCN–NaCN (53% by weight of NaCN), and this mixture was treated as described elsewhere for alkali cyanides.[4]

The zinc cyanide content of the salt phase after purification was determined by titrating a sample of the melt with ethylenediaminetetra-acetic acid (cyanide was removed by boiling it off as HCN using sulphuric acid), and was found to be $(9 \pm 0.1)\%$.

Zinc cyanide was added to the eutectic melt used in the present investigation in order to keep the composition of the salt phase constant during extractions with zinc alloys. It was found that better reproducibility was obtained with zinc cyanide-containing melts than with pure (Na,K)CN.

Metal Phase.—Laboratory-grade Bi, Sn, and Zn were further purified of oxide impurities by filtering through porosity-2 sintered glass filters under an argon atmosphere.

Radioactive Tracers.—Radioactive tracers were prepared by the neutron irradiation of Specpure metal or metal chlorides. ^{105}Rh tracer was obtained[5] from neutron-irradiated $RuCl_3$.

Containers.—Containers were constructed from titanium which was found not to react with either the melt or solutes.[4]

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

[2] K. F. Fouché, J. G. V. Lessing, and P. A. Brink, in 'Proceedings of International Solvent Extraction Conference, Lyon, September 1974,' Society for Chemical Industry, London, 1974, p. 2685.

[3] J. G. V. Lessing, K. F. Fouché, and T. T. Retief, following paper.

[4] J. G. V. Lessing, K. F. Fouché, and T. T. Retief, *Electrochim. Acta*, in the press.

[5] J. G. V. Lessing and K. F. Fouché, *Analyt. Chem.*, 1975, **47**, 182.

Thus, iridium tracer was kept in solution for >40 h without any detectable losses.

Extractions.—Extractions were carried out in an argon-filled glove box (<20 p.p.m. oxygen and <10 p.p.m. water). The crucible was positioned on the bottom of a stainless-steel tube which had its open end sealed to an opening in the glove box base, and its lower portion in a well-type furnace. The temperature of the furnace was controlled by a commercial electronic controller operating from a thermocouple placed outside the stainless-steel tube. The temperature of the melt (530 ± 3 °C) was obtained from a thermocouple adjacent to the crucible. Equilibrations were carried out by stirring the phases.

The metal tracer was dissolved in a weighed amount of salt phase (30 g), and the total activity was determined from the mean specific activity of five melt samples (*ca*. 0.2 g each) pipetted from the melt. Metal phase (10 g) was added, and the phases stirred until equilibrium was obtained. Although it was found that equilibrium was reached in <10 min (q_e remained constant within 5%), a minimum of 30 min was usually allowed. The specific activity of the salt phase (corrected for radioactive decay) was again determined before additions were made to the metal phase.

Because of the small volume of the metal phase (<2 ml) samples were not taken from this phase. The specific activity of the metal phase was instead calculated from the loss of activity that occurred in the salt phase upon introduction of a metal phase.

The experimentally determined distribution ratio, q_e

$$q_e = \frac{\text{specific activity of the metal phase}}{\text{specific activity of the salt phase}} = \frac{t_m}{t_s} \qquad (2)$$

[equation (2)], was transformed to the distribution constant,

$$q = \frac{\text{atom fraction of M in metal phase}}{\text{mol fraction of M(CN)}_m\text{ in salt phase}} = \frac{X_m}{X_{\mathrm{M(CN)}_m}} \qquad (3)$$

q [equation (3)], through the relation (4), where F is a function of the composition of the system (see Appendix). All

$$q = q_e F \qquad (4)$$

experimental values (q_e) were thus transformed to q, the experimental value of the distribution constant.

The variation in q_e with metal-phase composition and the magnitude of the factor F is shown in Table 1 where the experimental results are summarised.

RESULTS AND DISCUSSION

The distribution of a metal M in a system composed of a 9% solution of zinc cyanide in molten (K,Na)CN and a liquid zinc alloy is determined by the reversible reaction (5).

$$\underset{\text{Salt}}{\mathrm{M(CN)}_m} + \underset{\text{alloy}}{\frac{m}{2}\mathrm{Zn}} \rightleftharpoons \underset{\text{alloy}}{\mathrm{M}} + \underset{\text{salt}}{\frac{m}{2}\mathrm{Zn(CN)_2}} \qquad (5)$$

The distribution constant of M defined in equation (3) can be calculated from the thermodynamic equilibrium constant K_a of equation (5) as (6),[6] where a denotes

$$\log q = \log K_a + \left[\frac{m}{2}\log a_{\mathrm{Zn}} - \log \gamma_{\mathrm{M}}\right] \times \left[\frac{m}{2}\log a_{\mathrm{Zn(CN)_2}} - \log \gamma_{\mathrm{M(CN)}_m}\right] \qquad (6)$$

activities; $a = \gamma x$, and $\gamma \rightarrow 1$ if $x \rightarrow 1$, where x designates mole or atom fractions and γ activity coefficients. Most of the thermodynamic quantities in equation (6) are not known. This equation can, nevertheless, be simplified to a useful relationship as is shown below.

The terms in the first set of parentheses are functions of the composition of the metal phase only, and those terms in the second set of parentheses are determined by the salt phase only. If the composition of the salt phase is thus kept constant, equation (6) reduces to (7). The

$$\log q = \text{constant} + \frac{m}{2}\log a_{\mathrm{Zn}} - \log \gamma_{\mathrm{M}} \qquad (7)$$

composition of the salt phase can be regarded as constant when the distribution of a minute quantity of M is considered, since the composition of the phases will then not be affected significantly by the interphase mass transfer of M. Furthermore, since $x_{\mathrm{M}} \rightarrow 0$, the metal phase can be regarded as the binary alloy S–Zn (S = Bi or Sn), and values for a_{Zn} can thus be obtained from literature on binary alloys.[7]

The values for γ_{M} depend on the composition of the metal phase only, and can be calculated from the following approximation (8) given by Johnson[6] where $(\gamma_{\mathrm{M}})_{\mathrm{S}}$

$$\log \gamma_{\mathrm{M}} = x_{\mathrm{S}} \log (\gamma_{\mathrm{M}})_{\mathrm{S}} + x_{\mathrm{Zn}} \log (\gamma_{\mathrm{M}})_{\mathrm{Zn}} \qquad (8)$$

and $(\gamma_{\mathrm{M}})_{\mathrm{Zn}}$ are the activity coefficients of M (at infinite dilution) in pure S and Zn respectively. Johnson pointed out that fairly good approximations for γ_{M} can be obtained especially when the activity coefficients in the pure components differ by several orders of magnitude.

From equations (7) and (8), and since $x_{\mathrm{S}} = 1 - x_{\mathrm{Zn}}$

$$\log q - \frac{m}{2}\log a_{\mathrm{Zn}} = \text{constant} - \beta x_{\mathrm{Zn}} \qquad (9)$$

where

$$\beta = \log (\gamma_{\mathrm{M}})_{\mathrm{Zn}} - \log (\gamma_{\mathrm{M}})_{\mathrm{S}} \qquad (10)$$

Equation (9) predicts that if q is determined as a function of the composition of the metal phase (*i.e.* x_{Zn}), and $(\log q - \frac{m}{2}\log a_{\mathrm{Zn}})$ is plotted *vs* x_{Zn}, a straight line with slope $-\beta$ will be obtained.

The results (given in Table 1) thus plotted for the extraction of Ir ($m = 1$), Rh ($m = 1$), and Cu ($m = 1$)

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

[7] 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.

with Bi–Zn alloys, and Ir, Ru ($m = 2$), and Cu with Sn–Zn alloys are shown in Figures 1 and 2 respectively (the slopes are summarised in Table 2). The results are in good agreement with the expected behaviour for an exchange mechanism as given in equation (5).

TABLE 1

Distribution data for Rh, Ir, Ru and Cu between molten cyanide and liquid Bi–Zn and Sn–Zn alloys

Bi–Zn			
x_{Zn}	a_{Zn} *	log q_e	log q
		Ir	
0.201	0.524	−0.070	0.420
0.231	0.583	0.393	0.873
0.279	0.667	0.919	1.382
0.313	0.720	1.429	1.879
0.345	0.765	1.865	2.302
		Rh	
0.079	0.237	1.646	2.177
0.098	0.289	1.794	2.319
0.122	0.348	1.954	2.471
0.138	0.387	2.112	2.624
0.157	0.430	2.252	2.757
0.178	0.477	2.481	2.979
0.200	0.522	2.588	3.079
0.245	0.608	2.947	3.422
		Cu	
0.097	0.285	−0.697	−0.172
0.146	0.405	−0.636	−0.127
0.150	0.415	−0.584	−0.076
0.190	0.502	−0.366	0.128
0.227	0.575	−0.251	0.230
0.240	0.599	−0.188	0.289
0.294	0.691	0.001	0.458
0.388	0.820	0.389	0.809
0.456	0.892	0.510	0.902
0.550	0.968	0.814	1.163
1.000	1.000	2.253	2.302

Sn–Zn			
x_{Zn}	a_{Zn} *	log q_e	log q
		Ru	
0.401	0.624	0.195	0.418
0.500	0.708	0.266	0.465
0.599	0.782	0.364	0.537
0.698	0.838	0.497	0.642
0.801	0.881	0.447	0.562
		Ir	
0.010	0.018	0.312	0.620
0.022	0.028	0.562	0.867
0.023	0.030	0.580	0.363
0.036	0.050	0.912	1.274
0.047	0.074	0.877	1.178
0.058	0.102	0.941	1.239
0.070	0.136	1.086	1.382
0.081	0.167	1.339	1.633
0.093	0.195	1.308	1.599
0.144	0.237	1.554	1.841
0.126	0.258	1.748	2.032
0.143	0.287	1.908	2.189
		Cu	
0.156	0.324	0.702	0.980
0.180	0.343	0.715	0.988
0.203	0.380	0.917	1.185
0.304	0.516	1.024	1.269
0.401	0.624	1.214	1.437
0.506	0.724	1.353	1.550
0.606	0.794	1.549	1.720
0.683	0.822	1.698	1.848
0.772	0.871	1.836	1.961
0.898	0.933	2.092	2.177
1.000	1.000	2.316	2.366

* From ref. 7.

From equation (10) it can be seen that the value of β can be calculated from the values of γ_M in the two pure components. For the metals concerned, these values are known for copper only. The theoretical and experimental values of β_{Cu} are compared in Table 3. The agreement between the two sets of results is rather good and probably better than can be expected when considering that theoretical values were corrected for a 400 K difference between the literature data and the experimental results. The results can, however, be regarded as being in good support of an exchange-type mechanism when metal ions are extracted from molten cyanide with zinc alloys.

TABLE 2

Values for β_M obtained from a least-squares fit to the data in Table 1

	$-\beta$	
Element	Bi–Zn	Sn–Zn
Rh	6.38 ± 0.51	
Ir	12.28 ± 0.79	6.38 ± 1.70
Ru		0.28 ± 0.10
Cu	2.53 ± 0.16	1.29 ± 0.13

It further shows that extractions from molten cyanide can be utilised for the direct comparison of activity-coefficient ratios of platinum group metals in molten zinc relative to those in other liquid-metal solvents. Similar data cannot normally be obtained from other molten salt systems (*e.g.* halides) since platinum group metals are the more noble components of liquid-metal phases in such systems. Following the results given in Part 2,[3] measurements of activity-coefficient ratios can also be extended to systems not containing zinc.

TABLE 3

Comparison of the values of $-\beta_{Cu}$ experimentally determined in this investigation with the values calculated from equation (14) and literature [7] data for $(\gamma_{Cu})_{Bi}$, $(\gamma_{Cu})_{Sn}$, and $(\gamma_{Cu})_{Zn}$

	$-\beta_{Cu}$	
System	Experimental	Theoretical
Sn–Zn	1.29 ± 0.13	1.22
Bi–Zn	2.53 ± 0.16	2.60

Oxidation States of Metal Ions in Molten Cyanide Solution.—The oxidation states for Cu ($m = 1$) and Zn ($m = 2$) in molten cyanide are well established and have recently been confirmed by chronopotentiometry.[8] Molten cyanide solutions [9] as well as quenched melts [10] containing Rh, Ir, and Ru have recently been investigated spectroscopically and it was shown that Ru is present as Ru^{II} and that the most stable states for low concentrations of Rh and Ir are Rh^{I} and Ir^{I}. Concentrated solutions prepared from Rh^{III} and Ir^{III} salts may also contain a small fraction of the elements in the +3 oxidation state and evidence was presented for the existence, under certain conditions, of Rh^0 and Ir^0. The presence of Rh^{III} and Ir^{III} in some melts is due to incomplete reduction at high metal concentrations and the fraction of metal present in the high oxidation state rapidly decreases with concentration. It is, therefore, most unlikely that significant quantities of the high oxidation state species will be present in the tracer experiments described here. Any Rh^0 and Ir^0 species present in the melt will probably be unstable in the presence of liquid-metal phases such as Pb, Bi or Sn. It will, therefore, be transferred to the metal phase before zinc is added and will thus have no effect on the slope of extraction curves. The instability of the zero-valent complexes in the presence of liquid metals could not be proved directly, but seems most likely since it was found that $[Ni(CN)_4]^{4-}$, the most stable zero-valent metal cyanide complex identified so far, is immediately reduced to metal in the presence of the above liquid metals.[11]

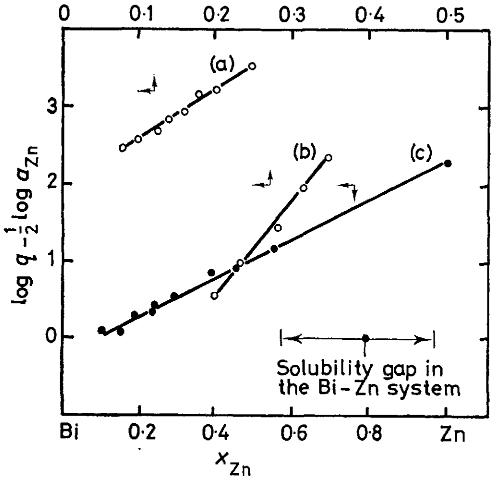

FIGURE 1 Results for the extraction of (a) Rh, (b) Ir, and (c) Cu from a 9% zinc cyanide solution with a Bi–Zn alloy

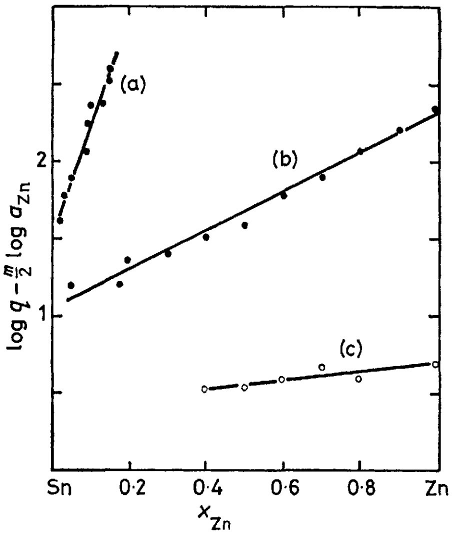

FIGURE 2 Results for the extraction of (a) Ir ($m = 1$), (b) Ru ($m = 2$), and (c) Cu ($m = 1$) from a 9% zinc cyanide solution with a Sn–Zn alloy

APPENDIX

Relation between q *and* q_e.—The following symbols are used:

X_i = mole or atom fraction of i
t_i = specific activity of i (counts kg^{-1} s^{-1})
G_i = mass of phase or component i
N_i = kg moles of i
A_i = atomic or molecular mass of i
i = m denotes the metal phase
i = s denotes the salt phase

Consider the distribution of Ir tracer in a system composed of a molten zinc cyanide solution and a binary zinc alloy Zn–S (S = Bi or Sn).

$$q_e = \frac{t_m}{t_s} \tag{A1}$$

$$q = \frac{X_{Ir}}{X_{IrCN}} \tag{A2}$$

For the metal phase

$$X_{Ir} = \frac{N_{Ir}}{N_{Ir} + N_{Zn} + N_S}$$

$$\simeq \frac{t_m G_m}{t_{Ir} A_{Ir}} \cdot \frac{1}{N_{Zn} + N_S} \quad (N_{Ir} \rightarrow 0) \tag{A3}$$

$$\text{but } G_m \simeq G_{Zn} + G_S \quad (G_{Ir} \rightarrow 0)$$
$$= N_{Zn}A_{Zn} + N_S A_S \tag{A4}$$

From (A3) and (A4)

$$X_{Ir} = \frac{t_m}{t_{Ir} A_{Ir}} \cdot (X_{Zn}A_{Zn} + X_S A_S) \tag{A5}$$

For the salt phase

$$X_{IrCN} = \frac{N_{IrCN}}{N_{IrCN} + N_{NaCN} + N_{KCN} + N_{Zn(CN)_2}}$$

$$\simeq \frac{t_s G_s}{t_{Ir} A_{Ir}} \cdot \frac{1}{N_{NaCN} + N_{KCN} + N_{Zn(CN)_2}}$$
$$(N_{IrCN} \rightarrow 0) \tag{A6}$$

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[8] E. T. van der Kouwe, unpublished results.

[9] K. S. de Haas and K. F. Fouché, *Inorg. Chim. Acta*, in the press.

[10] K. S. de Haas, K. F. Fouché, and C. M. Fouché, *Inorg. Chim. Acta*, 1977, **21**, 15.

[11] J. G. V. Lessing, unpublished results.

but

$$N_{\mathrm{NaCN}} + N_{\mathrm{KCN}} + N_{\mathrm{Zn(CN)_2}} = \frac{G_{\mathrm{NaCN}}}{A_{\mathrm{NaCN}}} + \frac{G_{\mathrm{KCN}}}{A_{\mathrm{KCN}}} + \frac{G_{\mathrm{Zn(CN)_2}}}{A_{\mathrm{Zn(CN)_2}}}$$

If the salt phase is composed of a fraction *a* of zinc cyanide in eutectic KCN–NaCN (53% by mass of NaCN), then

$$G_{\mathrm{Zn(CN)_2}} = \qquad \text{(A7)}$$

$$G_{\mathrm{NaCN}} = 0.53\,(1 - a)\,G_{\mathrm{S}} \qquad \text{(A7)}$$

$$\text{and} \quad G_{\mathrm{KCN}} = 0.47\,(1 - a)\,G_{\mathrm{S}} \qquad \text{(A7)}$$

From equations (A6) and (A7)

$$X_{\mathrm{IrCN}} = \frac{t_{\mathrm{S}}}{t_{\mathrm{Ir}} A_{\mathrm{Ir}} B} \qquad \text{(A8)}$$

$$\text{where } B = \frac{0.53\,(1 - a)}{A_{\mathrm{NaCN}}} + \frac{0.47\,(1 - a)}{A_{\mathrm{KCN}}} + \frac{a}{A_{\mathrm{Zn(CN)_2}}} \qquad \text{(A9)}$$

From equations (A2), (A5), and (A8)

$$q = \frac{t_{\mathrm{m}}}{t_{\mathrm{s}}} B\,(X_{\mathrm{Zn}} A_{\mathrm{Zn}} + X_{\mathrm{S}} A_{\mathrm{S}})$$

$$= q_{\mathrm{e}}\,F \qquad \text{(A10)}$$

$$\text{where} \quad F = B[A_{\mathrm{S}} + (A_{\mathrm{Zn}} - A_{\mathrm{S}})(X_{\mathrm{Zn}})] \qquad \text{(A11)}$$

i.e. F is a function of the composition of the salt phase (through B) and the composition of the metal phase (through X_{Zn}).

The values for F for Bi–Zn and Sn–Zn systems can thus be calculated from the following expressions.

$$\text{Bi–Zn} : F = 3.59 - 2.47\,X_{\mathrm{Zn}} \qquad \text{(A12)}$$

$$\text{Sn–Zn} : F = 2.04 - 0.92\,X_{\mathrm{Zn}} \qquad \text{(A13)}$$

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