SOLVATION OF IONS.   APPLICATIONS TO MINERALS AND ENERGY

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Abstract – Dimethylsulfoxide and acetonitrile have advantages over water
for faster organic reactions and for cheaper methods of refining copper,
silver and gold. Sulfur in dimethylformamide can be reduced to give CdS
films showing photogalvanic effects. Non-aqueous solvents have
applications in zinc-bromine batteries. A low cost-low energy method for
extracting copper from concentrates via the steps of a double roast, an
acetonitrile leach and thermal disproportionation is described.

INTRODUCTION

Solvents other than water offer solutions for many technological problems facing the minerals
and energy industries (Ref. 1). Technologists should appreciate that by comparison with
water, non-aqueous solvents offer different anion and cation solvating properties, different
solvation of uncharged solutes, different rates of reaction, different temperature ranges for
their liquid states, different ion mobilities and conductance, different acidities and
basicities, different redox stability, different densities, and different availability,
hazards and costs. How can these differences be used as a basis for new technological
concepts in energy storage, extractive metallurgy and metals recycling?

The anion-solvating properties of dipolar aprotic solvents like dimethylsulfoxide,
acetonitrile, dimethylformamide and propylene carbonate only began to be appreciated by most
chemists after a review which I wrote in 1960 (Ref. 2). This appreciation lead to a small
revolution in organic synthesis, because many bimolecular reactions of anions with carbon
compounds proved to be millions of times faster, in such solvents, than they were in
previously used solvents, like alcohols and water-organic mixtures (Ref. 3). Not only were
reactions faster, but products were much cleaner. This was because many of the unwanted
competing carbocation reactions which plague organic synthesis, were not accelerated to the
same extent by solvent transfer (Ref. 4).

Since returning to Western Australia, my interests have changed from organic chemistry to the
chemical aspects of minerals and energy. By describing a few discoveries made at Murdoch
University, I hope to show extractive metallurgists how the same solvents suggest new cheap
low energy processes for recycling and extracting gold, copper and silver. Electrochemists
may learn how such solvents offer advantages for load-levelling zinc-bromine batteries, for
lithium batteries in electric vehicles and for solar cells.

DISCUSSION

Rates of reaction
Why are associative reactions like (1) much faster in solvents which do not have hydrogens
available for H-bonding (e.g. DMF and DMSO).

$$Y^- + RX \; \rightleftarrows \; YRX^{-\ddagger} \; \rightarrow \; \text{Products} \tag{1}$$

The explanation (Ref. 3) is that larger anions, like transition state anions ($YRX^{-\ddagger}$) and
unlike small reactant anions (Y^-), are poor hydrogen-bond acceptors. Thus transition state
anions are as well solvated by DMF and DMSO as they are by hydrogen bond donors, such as the
hydroxylic solvents. On the other hand, smaller reactant anions, Y^-, being stronger H-bond
acceptors, are more strongly solvated by hydroxylic solvents, than by DMF or DMSO.

The kinetic implications are shown in Figure 1, where we see that the free energy changes
$\Delta G_{tr} Y^-$ and $\Delta G_{tr} YRX^-$ of anions of different size, upon solvent transfer from hydroxylic
solvents, lead to a lower free energy of activation and thus faster associative reactions (1),
in DMF and DMSO. Obviously the stronger the H-bond acceptor properties of the reactant
anion, Y^-, the greater the rate enhancement upon solvent transfer. Thus associative

reactions of F^-, Cl^- and OH^- are accelerated more than are reactions of I^-, SCN^- and SH^-. In general, changes in the free energy of RX on solvent transfer are small enough to ignore. Indeed, the linear free energy relationship, $\Delta \log k = n\Delta G_{tr}Y^-$, adequately predicts the degree of rate enhancement of most reactions (1) of carbon compounds.
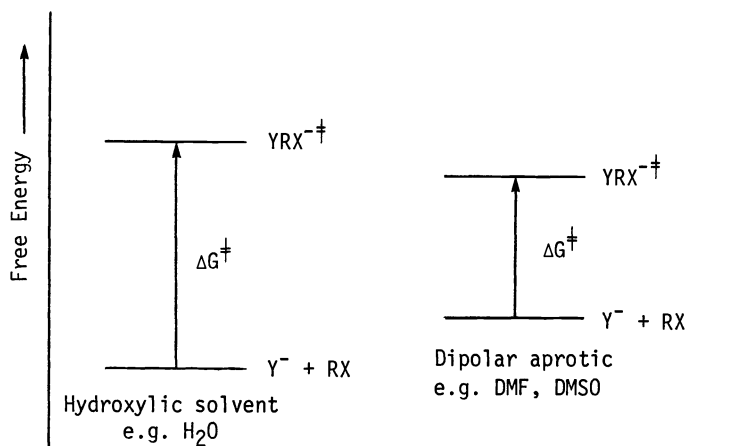

Fig. 1.   Solvent effects on rates of associative reactions.

Anion and cation solvating properties of solvents (Refs 5,6)

Single ion thermodynamic properties, for transfer of ions between solvents, are of value to the technologist. Many of us record such properties via the following TATB assumption (Ref. 7):

$$\Delta G_{tr}Ph_4As^+ = \Delta G_{tr}Ph_4B^-; \quad \Delta H_{tr}Ph_4As^+ = \Delta H_{tr}Ph_4B^-; \quad \Delta S_{tr}Ph_4As^+ = \Delta S_{tr}Ph_4B^-;$$

$$\Delta V_{tr}Ph_4As^+ = \Delta V_{tr}Ph_4B^-; \quad \Delta \lambda_{tr}Ph_4As^+ = \Delta \lambda_{tr}PhB^-.$$

The cation solvating power (CSP) of solvents at 25° is indicated by $-\Delta G_{tr}K^+$ (TATB) or by changes in the donor number (ΔDN) (Ref. 5) of the solvent. The linear free energy relationship (2) gives us likely free energies of transfer of many cations (M^{n+}) through many

$$CSP = -p\Delta G_{tr}K^+ = 1.3\ p\Delta DN = -\Delta G_{tr}M^{n+} \tag{2}$$

solvents, provided that the sensitivity parameter p of the cation M^{n+} is known, or can be estimated. Deviations from (2) reveal specific cation-solvent interactions.

The anion solvating power (ASP) of solvents at 25° is indicated by $-\Delta G_{tr}Cl^-$ (TATB), or by changes in the solvent acceptor number (ΔAN), or by changes in the solvent transition energy (ΔE_T) (Ref. 8). Free energies of transfer of anions are given by relationship (3). We have not encountered serious deviations from (3), as we do for some cations in (2).

$$ASP = -m\Delta G_{tr}Cl^- = 1.3\ m\Delta AN = 0.63\ m\Delta E_T = -\Delta G_{tr}A^{n-} \tag{3}$$

Values of $\Delta G_{tr}K^+$, $\Delta G_{tr}Cl^-$, ΔDN, ΔAN and ΔE_T for transfer between various solvents are in Table 1. Some free energies of transfer of cations which I use, but have not published, are in Table 2. They were calculated from reported solubilities, or from ($E^o_{M+} - E^o_{K+}$) and ($E_{\frac{1}{2}}M^+ - E_{\frac{1}{2}}K^+$) for reversible electrochemical systems. They allow estimates of the sensitivity parameters p in equation (2).

As shown elsewhere (Ref. 6), cation and anion solvating power is determined by Born solvation, hydrogen-bonding, d^{10}-π^* back bonding, Lewis acid-base interaction, structure making and structure breaking and the nebulous, but useful, hard-soft-acid-base interactions.

Kinetic aspects (Refs 9,10)

Kinetic consequences of ion solvation are as important as thermodynamic, but time allows me only to say that electron transfer in the Cu^{2+}/Cu^+ couple in acetonitrile-water mixtures is faster than with the aqueous Fe^{3+}/Fe^{2+} couple on a variety of surfaces. Diffusion coefficients vary for ions with different solvation shells in solvents of various viscosities. Overpotentials in the Li/Li^+ system seem less in the presence of acetonitrile than in propylene carbonate. These observations have implications for oxidative leaching with Cu^{2+} or Fe^{3+} salts and for lithium batteries.

Solution thermodynamics of hydrometallurgical interest (Ref. 9)

Table 3 shows equilibrium constants and entropy changes for a variety of equilibria involving copper and silver ions in acidified water and in 6 M solutions of acetonitrile in acidified

TABLE 1. Ion solvating properties and donor and acceptor properties of solvents at 25°. Transfer from DMF.[a]

| Solvent | CATION SOLVATING | | ANION SOLVATING | | |
| | $-\Delta G_{tr}K^+$ | ΔDN^c | $-\Delta G_{tr}Cl^-$ | ΔAN^c | $\Delta E_T{}^b$ |
	kJ mol^{-1}		kJ mol^{-1}		
CF_3CH_2OH	-45	-	+56	37	66
H_2O	-9	-9	+46	39	81
$HCONH_2$	-7	-	+33	24	54
MeOH	-18	-8	+32	25	49
NMeF	-	-	+25	16	43
EtOH	-25	-	+25	21	34
Me_2SO	+3	-24	+6	4.5	10
$MeNO_2$	-31	+3	+14	3	5
P.Carb.	-12	-11.5	+4	2	12
MeCN	-19	-12.5	+4	3	9
TMS	-15	-12	+4	-	1
DMF	0	0	0	0	0
Py	-	6	-	-2	-4
DMA	+2	1	-3	-2	-1
NMePy	+1	1	-3	-3	-7
Me_2CO	+11	-10	-11	-3.5	-7
HMPT	+8	12	-13	-5	-35
SMDF	-37	-	-	-	-
C_6H_5CN	-22	-15	-	-	-8

Cation solvating $= -\Delta G_{tr}M^{n+} = -p\Delta G_{tr}K^+ = +1.3\ p\Delta DN$

Anion solvating $= -\Delta G_{tr}A^- = -m\Delta G_{tr}Cl^- = +1.3\ m\Delta AN = +0.63\ m\Delta E_T{}^b$

a. Reference 4.   b. Reference 8.   c. DN and AN are Gutmann's donor numbers and acceptor numbers respectively.

TABLE 2. Cation solvating power (TATB assumption) at 25°. $\Delta G_{tr}M^+$ kJ mol^{-1} from water.[a]

Solvent	Ph_4As^+	Li^+	Na^+	K^+	Rb^+	Tl^+	Ag^+	Ba^{2+}	Zn^{2+}	Cd^{2+}	Cu^{2+}
H_2O	0	0	0	0	0	0	0	0	0	0	0
MeOH	-23	4	8	9	10	5	7	18	28	33	-
EtOH	-23	6	15	14	13	-	3	43	-	-	-
PhCN	-	36	23	13	11	-	-17*	58	66	53	-
MeCN	-33	30	18	10	7	7	-22*	57	69	42	68
DMSO	-39	-15	-13	-12	-8	-22	-34	-38	-49	-54	-42
DMF	-38	-10	-9	-9	-9	-14	-17	-36	-30	-32	-25
PC	-36	24	17	7	9	8	16	29	46	35	73
SDMF	-	54	41	28	14	-19	-104*	-	-14	-40	-
HMPT	-39	-	-39	-15	-11	-16	-43	-	-54	-52	-38
$HCONH_2$	-24	-8	-6	-4	-2	-10	-15	-	-18	-16	-28
NMePy	-40	-	-11	-9	-5	-15	-24	-37	-18	-26	-16
TMS	-34	21	10	6	2	4	7	38	88	65	-
Me_2CO	-27	-	-10	2	1	3	8	23	42	48	-
CF_3CH_2OH	-	-	-	36	-	-	49	-	-	-	-
NMeF	-	-15	-8	-8	-8	-	-	-	-	-	-

* Specific interaction (back bonding).

a. A.J. Parker, unpublished literature survey.

TABLE 3. Equilibria involving copper and silver ions in water and in acetonitrile-water at 25°C.

Equilibrium	log K H_2O	log K 25% An[a]	$-298 \Delta S_{tr}$ H_2O to 5.7% An[a] kJ mol^{-1}
$Cu^{2+} + Cu^0 \rightleftharpoons 2Cu^+$	-6.2	+9.4	75.5
$Cu^{2+} + Ag^0 \rightleftharpoons Cu^+ + Ag^+$	-10.8	+0.3	49.0
$Cu^{2+} + CuS \rightleftharpoons 2Cu^+ + S$	-15.5	+0.1	75.5
$Cu^{2+} + Cu_2S \rightleftharpoons CuS + 2Cu^+$	-12.2	+3.3	75.5
$Cu^{2+} + Fe^{2+} \rightleftharpoons Cu^+ + Fe^{3+}$	-10.4	-1.6	31.7

a. In mole % acetonitrile shown, data from reference 7.

water (Refs 1,9). Equilibrium lies much more strongly to the right in acetonitrile-water mixtures than in water, because of strong specific back-bonding interactions ($d^{10}-\pi^*$) of these d^{10} cations with the $-C\equiv N$ group of acetonitrile (Ref. 1). Values of K increase with increasing concentration of acetonitrile.

Values of ΔG_{tr} and ΔH_{tr} for transfer of Cu^+ and Ag^+ from water to acetonitrile-water mixtures (Table 4) are negative. There is a loss of entropy on such transfer (Table 4). This is a consequence of exchanging water by hydrophobic acetonitrile in the solvation shell of these d^{10} cations. Cations which are not d^{10} (e.g. Na^+, Cu^{2+}, Fe^{3+}, Fe^{2+}) show different solution thermodynamics because they have water in their solvation shells both in water and in 6 M acetonitrile-water. The different composition of the solvation shells leads to interesting entropies of transfer for some of the equilibria in Table 3 and for the ions in Table 4, as shown.

TABLE 4. Thermodynamic functions[a] (kJ mole^{-1}) (TATB) for transfer of ions from water to 5.7 mole % acetonitrile-water at 25°.

	ΔG_{tr}	ΔH_{tr}	$-298 \Delta S_{tr}$
Cu^+	-27.8	-71.6	43.8
Ag^+	-7.3	-24.9	17.6
Na^+	+1.1	-2.8	3.6

a. From reference 9.

The hydrometallurgical interest in the equilibria of Table 3 is that one can separate concentrated (1 M) solutions of Cu_2SO_4 and Ag_2SO_4 from unwanted insolubles, by leaching materials, containing impure copper and silver, in acidified acetonitrile-water mixtures (Refs 1,11). If low boiling acetonitrile is then distilled from the aqueous solution, copper or silver crystallises, because equilibria (4) or (5) are well to the left in the absence of acetonitrile in aqueous solution.

$$Cu^0 + CuSO_4 \rightleftharpoons Cu_2SO_4 \qquad\qquad (4)$$

$$2Ag^0 + 2CuSO_4 \rightleftharpoons Ag_2SO_4 + Cu_2SO_4 \qquad\qquad (5)$$

Thermal disproportionation

The reversal of reaction (4) by distilling acetonitrile is known as thermal disproportionation of copper(I). It proves to be an excellent method of recovering high purity particulate copper from solutions of copper salts. In the method, a 50/50 water-acetonitrile vapour is rapidly stripped at 80-95°C from 1 M Cu_2SO_4 at pH 2 in 6 M acetonitrile. Lower temperatures are possible at reduced pressures. Low grade 25 psig saturated steam is a suitable heat source. Stripping is in a multiple effect stripping column and is preceded by partial flash evaporation. It is followed by fractionation of the vapour to give azeotropic (85%) acetonitrile-water as tops and pure water (for washing the precipitated copper) as bottoms. Copper powder precipitates and the solution turns blue as stripping proceeds. Steam consumption is 13,000-16,000 kJ/kg copper powder produced. The resulting copper is of

exceptional purity (Ref. 11). One can appreciate that there are advantages of using waste steam, with a very fast copper recovery, than in using high grade electrical energy (7000 kJ/kg copper) in the more familiar, but slower and capital-intensive, electrochemical process for winning copper from $CuSO_4$ solutions in water. The advantage is especially apparent when processes further upstream (e.g. roasting of sulfides) provide the heat for steam generation, as in the roast-leach-disproportionation process (Refs 13,14) or the double roast-leach-disproportionation process (Refs 14,15), for sulfide concentrates. An alternative to thermal disproportionation is electrochemical disproportionation (Ref. 11), which requires ca. 1000 kJ/kg copper of electrical energy. Here Cu_2SO_4 solutions, in acidified acetonitrile-water, are electrolysed at an insoluble anode and a copper cathode.

<u>Copper(II) as an oxidant.</u> $CuSO_4$ is a powerful oxidant in 6-10 M acetonitrile. Its reduction potential for reaction (6) is $0.5-0.6$ volt in 6-10 M acetonitrile (Ref. 16). Thus

$$Cu^{2+} + e^- \rightarrow Cu^+ \tag{6}$$

it can replace $FeCl_3$ and ferric sulfate in water as an oxidant for leaching cement copper, segregated copper, blister copper, electrolytic powders, copper sulfides, scrap copper, copper-nickel mattes, leady matte, circuit boards and brasses and bronzes (Ref. 11). Electron transfer is faster to Cu^{2+} in these corrosion processes than to iron(III). Since copper(II) oxidises copper materials in the leaches, no extra foreign ions are introduced to the solutions if $CuSO_4$ is used. Pure copper metal is recovered by thermal or electrochemical disproportionation of Cu_2SO_4. The $CuSO_4$ also formed is recycled, together with the acetonitrile azeotrope. The oxidative leach continues. A bleed stream controls the build up of soluble impurities and of wash water in the circulating electrolyte.

<u>Process concepts.</u> Some ideas (Refs 1,11) for continuously processing materials containing copper or silver are illustrated in Figure 2. They are based on the concept of leaching the metals with strongly oxidising $CuSO_4$ in acetonitrile-water, then thermally (or electrochemically) disproportionating the resulting Cu_2SO_4 solution, with recycle of $CuSO_4$ and acetonitrile. The most promising concept is to use the scheme to refine scrap copper, cement copper or reduced copper from roasted chalcopyrite.
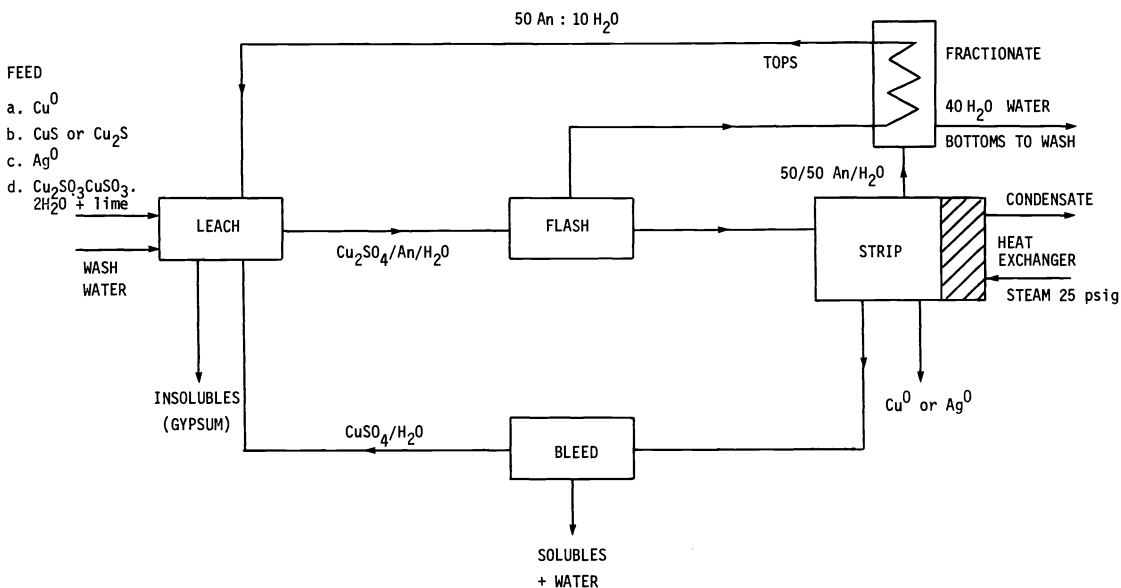
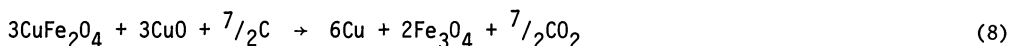

Fig. 2. Process concept for copper and silver refining.

<u>Commercial consideration.</u> Acetonitrile is available in large quantities as a wet, moderately toxic, inflammable, cheap by-product of the SOHIO process for acrylonitrile. Allowable vapour levels are about double those for toxic ammonia, which is widely used in hydrometallurgy. Acetonitrile-based copper recovery is fast and low pressure steam is the energy source. Stainless steel is adequate for containing the sulfate-nitrile system. Copper containing *less than 1 ppm of any element* other than copper, sulfur and oxygen has been refined from Mt Isa blister copper, via the nitrile process (Ref. 11). Water balance problems are accommodated by the concept of stripping a 50/50 vapour then fractionating to the 84/16 azetrope. Operating and capital costs for a leach-disproportionate-wire bar continuous system (Fig. 2) are estimated to be notably less than for an electrolytic copper refinery.

A process for copper concentrates.   The chemistry discussed above leads to a low energy process for recovering copper from chalcopyrite (Refs 14,15). The steps are as follows.
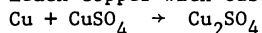
- Oxidatively dead roast chalcopyrite at 900°C, collect heat as steam (Ref. 17).

$$2CuFeS_2 + {}^{13}/_2O_2 \rightarrow CuFe_2O_4 + CuO + 4SO_2 \tag{7}$$
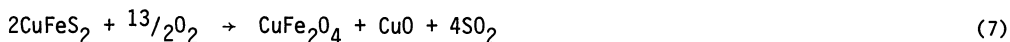
- Reductively roast, possibly under segregation conditions (Refs 18,19)

$$3CuFe_2O_4 + 3CuO + {}^7/_2C \rightarrow 6Cu + 2Fe_3O_4 + {}^7/_2CO_2 \tag{8}$$

- Leach copper with $CuSO_4$ in acetonitrile-water (Ref. 15).
  $Cu + CuSO_4 \rightarrow Cu_2SO_4$

- Thermally disproportionate the Cu_2SO_4 solution, using steam from the roaster. Recover pure copper (Ref. 15). $Cu_2SO_4 \rightarrow Cu + CuSO_4$

- Collect segregated gold and silver by screening leached oversize carbon particles (Ref. 15), by cyanidation, or by acid dissolution of magnetite.

This concept could require less than 50% of the energy and less than 60% of the capital cost of any operating pyrometallurgical process (Ref. 20). Note that the highly exothermic oxidation of chalcopyrite is the energy source for low grade steam, which is used in the distillation. Distillation is the major energy consumer in the process.

Processing of gold and silver (Refs 21,22).   Because of anion solvating properties (Fig. 1) chloro complexes of copper(I), gold(III) and silver are very much more stable in dry DMSO than in water. Thus copper(II) chloride is a very powerful oxidant (E^o 0.6 V) in the presence of NaCl or $CaCl_2$ in DMSO. Forward reactions (9) - (14) occur rapidly, to give high concentrations of copper, silver and gold complexes in dry DMSO (Table 5).

$$AgCl + NaCl \rightleftharpoons AgCl_2^- + Na^+ \tag{9}$$

$$Ag + CuCl_2 + 2NaCl \rightleftharpoons CuCl_2^- + AgCl_2^- + 2Na^+ \tag{10}$$

$$Ag_2S + 2CuCl_2 + 4NaCl \rightleftharpoons 2AgCl_2^- + S + 2CuCl_2^- + 4Na^+ \tag{11}$$

$$Ag_2Se + 2CuCl_2 + 4NaCl \rightleftharpoons 2AgCl_2^- + Se + 2CuCl_2^- + 4Na^+ \tag{12}$$

$$Au + 3CuCl_2 + 4NaCl \rightleftharpoons AuCl_4^- + 3CuCl_2^- + 4Na^+ \tag{13}$$

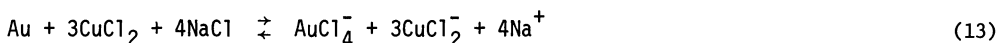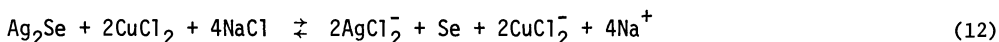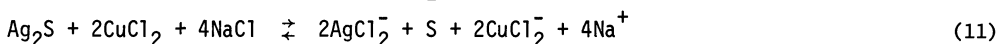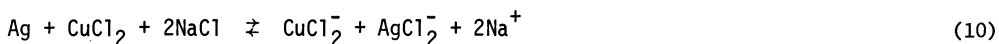$$Cu + CuCl_2 + 2NaCl \rightleftharpoons 2CuCl_2^- + 2Na^+ \tag{14}$$

TABLE 5.   Dissolution of silver and gold in DMSO-chloride solutions at 25°.

Equilibrium	log K^a H_2O	log K^b DMSO	$[M^+]^c$ g/l
$Cu^{2+} + Ag^0 + 4Cl^- \rightleftharpoons CuCl_2^- + AgCl_2^-$	-0.5	+19	100
$3Cu^{2+} + Au^0 + 10Cl^- \rightleftharpoons 3CuCl_2^- + AuCl_4^-$ ^{d}	-28.1	+19	80
$2Cu^{2+} + Ag_2S + 8Cl^- \rightleftharpoons 2CuCl_2^- + 2AgCl_2^- + S$	-7.6	+32	-

a. Stability constants - Special Publication 17, The Chemical Society.
b. Approximate value calculated from water values and $\Delta G_{tr}Cl^- = +40$ kJ mol^{-1} (Table 1), $\Delta G_{tr}Cu^{2+} = -42$ kJ mol^{-1} (Table 2), $\Delta G_{tr}AgCl_2^- = +4$ kJ mol^{-1} (Ref. 3) and assuming $\Delta G_{tr}CuCl_2^-$ and $\Delta G_{tr}AuCl_4^-$ are $+4$ kJ mol^{-1} as for $\Delta G_{tr}AgCl_2^-$. More precise measurements are in progress.
c. Concentration of gold or silver which dissolves in dry DMSO containing 2 M $CaCl_2$ and 1 M $CuCl_2$.
d. Assumed species, work in progress.

An interesting aspect is that oxidation of silver materials in _aqueous_ chloride solutions (e.g. with $FeCl_3$) leads to a film of AgCl, which partly passivates further oxidation. In dry DMSO, an AgCl film does not form. This is because $NaAgCl_2$ is soluble and stable in DMSO, so that oxidation of silver and its derivatives takes place orders of magnitude faster with $FeCl_3$ or $CuCl_2$ in dry DMSO than with $FeCl_3$ in water.

When water or other protic solvent is added to DMSO solutions of $AgCl_2^-$ or $CuCl_4^-$ containing $CuCl_2^-$ (Ref. 21), reactions (9) – (12) precipitate silver chloride (15). This is because of

$$AgCl_2^- \rightarrow AgCl + Cl^- \tag{15}$$

the strong solvation of Cl^- by water and the resulting instability of the $AgCl_2^-$ complex in the presence of water. Reaction (13) precipitates gold metal (16) when water is added

$$AuCl_4^- + 3CuCl_2^- \rightarrow Au + 3CuCl_2 + 4Cl^- \tag{16}$$

(Ref. 23). This chemistry leads to the process shown in Figure 3 (Refs 22,23) for processing high grade materials containing gold or silver and sometimes copper. Such materials include cement silver, silver halide residues, circuit boards, coinage, photographic residues, precipitated gold, anode slimes and alloys containing gold or silver. The concept is well suited to "backyard operations" since no pyrometallurgical step is needed.
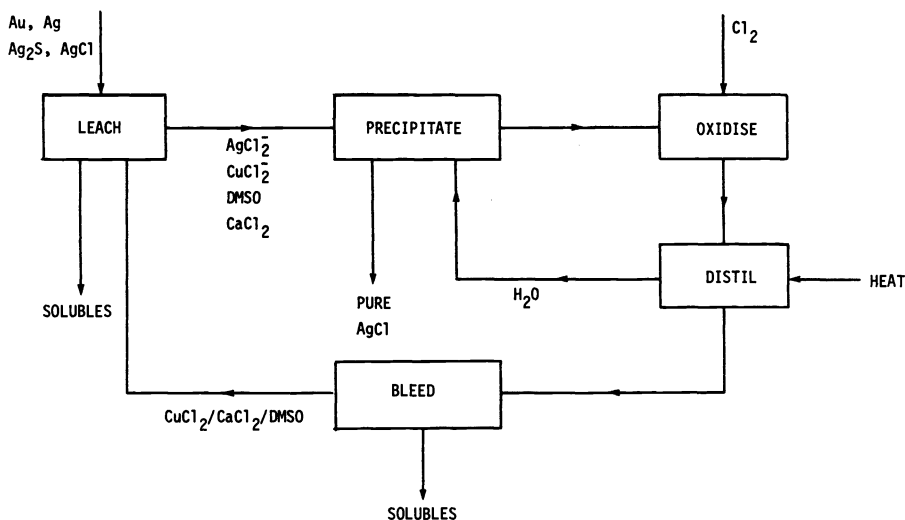

Fig. 3.   Process concept for gold and silver refining.

The zinc-bromine battery.   The zinc-bromine battery has great potential for solving current problems of load levelling, provided that the difficulties associated with chemical dissolution of zinc by dissolved bromine, dendrite formation and hydrogen evolution during recharging can be solved (Ref. 24). The battery is most promising as a fuel cell for electric vehicles.

We have found (Ref. 10) that a zinc-bromine battery, operating as shown in Fig. 4, with a two phase electrolyte containing bromine, zinc bromide, a dipolar aprotic solvent and water operates at an overall energy (coulombic × voltage) efficiency of ca. 60%, at a charge/discharge current density of 20 mA cm^{-2}, with electrode separation of 0.75 cm on an 8 hour charge – 8 hour discharge cycle. This is an excellent efficiency. Short circuit currents
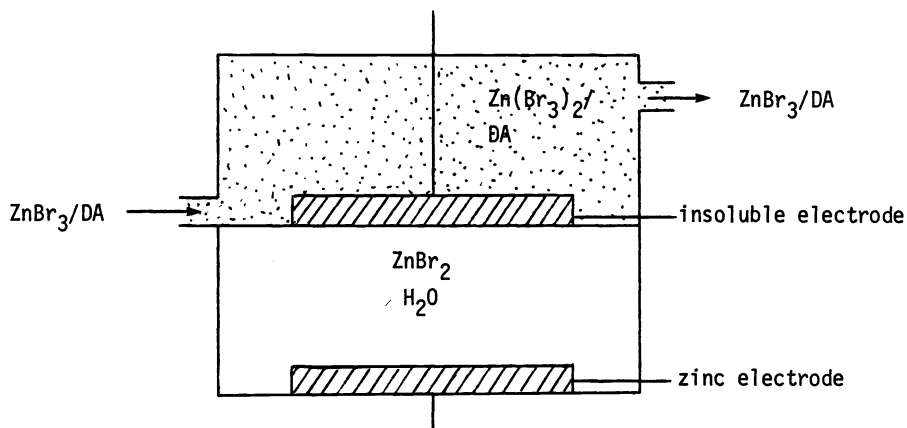

Fig. 4.   Zinc-bromine cell.

> 100 mA cm^{-2} without polarization over 30 minutes and the open circuit voltage is 1.76 volts. The two phase solvent keeps most of the bromine away from zinc. The solvent has no detectable reaction with bromine over 3 weeks. Our choice of solvent for this battery was influenced by the higher stability of polybromide complexes and the stronger solvation of Br_3 and Br_2 than in water (Refs 2,3). The high dielectric constant and low viscosity leads to low internal cell resistance. The partial miscibility of the solvent with water is important because hydrated zinc ions are well solvated in both the organic-rich phase and the aqueous phase. The lower density of the dipolar aprotic allows the zinc electrode and heavier water to be at the bottom of the cell and this assists with zinc deposition problems.

Acetonitrile for lithium batteries (Ref. 10). Lithium batteries offer excellent energy to weight ratios for electric vehicle applications. Electrolyte solutions must be inert to lithium and of high conductivity. In early work, $LiClO_4$ in propylene carbonate was the electrolyte of choice, but its high viscosity (2.53 cp) and thus low conductivity ($\Lambda_0 LiClO_4$ 5.4) are a drawback, despite the stability of lithium in propylene carbonate and lead to high overpotentials (iR effects).

We find that lithium salts in solvents containing acetonitrile have greater conductance (25 S) and better polarisation characteristics for lithium batteries than $LiClO_4$ in propylene carbonate.

Cadmium sulfide for photovoltaic devices. There is considerable interest in CdS/Cu$_2$S solar cells. Cadmium sulfide films in redox solutions exhibit photogalvanic effects. Films of polycrystalline CdS are made by vapour phase deposition. It may be more acceptable to make such films by electrochemical methods. Anodic growth by oxidising cadmium in sulfide media gives only very thin films, but we find (Ref. 25) that cathodic growth onto metal substrates is possible by electrolysing cadmium salts in DMF containing sulfur at temperatures above 110°C. The films are of good quality and exhibit photogalvanic effects in aqueous Na_2S solutions of ca. 500 mA cm^{-2} when irradiated with 80 watts cm^{-2} white tungsten light. Their thickness is 1-3 microns, which is too thin for formation of CdS/Cu$_2$S cells by conventional dipping in CuCl solutions, but is acceptable for photogalvanic redox systems.

The good sulfur-solvating and Cd^{2+}-solvating properties of DMF, its high boiling point, its lack of reducible hydrogen and electrochemical stability are qualities which make this dipolar aprotic solvent especially suitable for growth of metal chalcogenide films by reduction of sulfur and metal ions.

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