142. *The Equilibrium between Cuprous and Cupric Compounds in Presence of Metallic Copper.*

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Many cuprous salts tend to decompose into the cupric salt and copper, thus exemplifying one of the types of instability shown by particular valency states of some metals. The factors governing this instability and the equilibrium between cuprous and cupric compounds in solution in presence of copper have been investigated. The chief controlling factor appears to be the degree of covalency or electrovalency of the bonding between the copper ions and neighbouring ions or molecules, which is mainly dependent on the polarisability of the latter. Theory indicates that decreasing electrovalency and increasing covalency should favour the relative stability of the cuprous state, and experimental investigation of the equilibrium under various conditions confirms this.

The stabilisation of valency states by formation of complex ions (*e.g.*, of Co^{+++} in cobaltammines, etc., of Mn^+ and Ni^+ in complex cyanides, of Cu^{++} by ethylenediamine) has received but little systematic study. Instability of a valency state of a metal is nearly always attributable to (1) oxidation or reduction of the metal ions by the anion or other substance present (*e.g.*, water), or (2) interaction of the metal ions giving ions of higher valency plus the metal; *e.g.*, in cuprous and cupric compounds, the controlling factors, as far as the metal ions are concerned, are the energy changes in the reactions

$$Cu^{II} + \epsilon \rightleftharpoons Cu^{I} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$2Cu^{I} \longrightarrow Cu^{II} + Cu \text{ (solid metal)} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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* This dilution was determined by the small quantity of 2 : 4 : 5-trichloroacetophenone available, since identical molar concentrations were maintained throughout the comparative series. The large differences in the basic strengths of 2 : 4 : 5- and 2 : 4 : 6-trimethylacetophenones were confirmed with more concentrated solutions, which gave larger differentiation in the $n_D^{20°}$ values.

where Cu^{II} and Cu^{I} represent the ions in solid salts or in solution. Reaction (2) is of interest since it is the only common example in which the equilibrium between the two valency states and the metal is conspicuously changed by relatively slight changes in the groups co-ordinated with the ions. It is considered in some detail in this paper, but to confine the discussion to the so-called " complex " compounds alone is an artificial restriction. The natural scope of such a study is the stability of cuprous compounds in general, whether solid, or in solution as simple or complex ions. Reaction (1) will not be dealt with separately, but is, of course, involved in reaction (2). The influence of the immediate environment of the ions on the free-energy change in reaction (1) could be treated by the methods to be used for reaction (2), and would be theoretically simpler, but the experimental investigation would have to depend on rather unsatisfactory oxidation–reduction potential measurements.

A general consideration of cuprous salts shows that those which decompose very easily according to reaction (2) (*e.g.*, the sulphate and fluoride) or which are too unstable to be prepared (*e.g.*, the nitrate and perchlorate) are, or would be, predominantly ionic. On the other hand, the simple cuprous salts that are stable are all sparingly soluble in water and are regarded as having in the crystal a considerable proportion of covalent bonding. In the case of the halides, evidence for this is supplied by the experimental values for the lattice energies and interionic distances (cf. Rice, " Electronic Structure and Chemical Binding," pp. 238, 335, McGraw Hill, 1940; Sherman, *Chem. Rev.*, 1932, **11**, 153). Cuprous fluoride, which would be the most ionic of the halides, is unstable, decomposing into cupric fluoride and copper, and has not been prepared pure (von Wartenburg, *Z. anorg. Chem.*, 1939, **241**, 381). This suggests that the energy change accompanying reaction (2), and hence the stability of cuprous compounds in general, may be related to the nature of the bonding between the cuprous ion and the neighbouring ions or atoms. The object of this paper is to attempt an interpretation on these lines.

The basic reaction in the decomposition of a cuprous compound is

$$2Cu^{+} \longrightarrow Cu^{++} + Cu \text{ (solid metal)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where Cu^{+} and Cu^{++} represent isolated ions or ions in the gas phase. For this reaction $\Delta U = +\ 207{\cdot}7$ kg.-cals., $\Delta H = +\ 207{\cdot}1$ kg.-cals., and ΔG° (gaseous ions at a concentration of 1 g.-ion/l.) = 214·3 kg.-cals., all at 25° (the heat of sublimation of copper being taken as 81·5 kg.-cals. at 25°). This indicates a considerable absorption of energy, which will be largely modified when the process occurs in solution or in a solid compound, as in (2), on account of the bonding, or interaction, energy between the copper ions and neighbouring ions or molecules. The latter energy constitutes, in a crystal, the lattice energy, and in a solution of the simple ions, their solvation energy. For so-called complex ions in solution, the energy of the bonding of the ion to the co-ordinated groups constitutes the greater part of the total interaction energy. The interaction energy may be regarded as a change in the energy of the ion from that of the free ion in the gas phase as a standard, and will be called U^{I} or U^{II} (for Cu^{+} or Cu^{++}). Since it is a lowering of energy, U^{I} and U^{II} will be negative. So we have for reactions (3) and (2),

$$2Cu^{+} \longrightarrow Cu^{++} + Cu \text{ (solid metal)}; \ \Delta U = +\ 207{\cdot}7 \text{ kg.-cals.}$$
$$2Cu^{I} \longrightarrow Cu^{II} + Cu \text{ (solid metal)}; \ \Delta U' = 207{\cdot}7 + (U^{II} - 2U^{I}) \text{ kg.-cals.} \quad . \quad (4)$$

The bonding between the copper ions and neighbouring ions or atoms may be almost purely ionic or covalent or intermediate [continuous transition between the two types is possible, since the number of unpaired electrons in both cuprous and cupric ions (0 or 1) is the same for either electrovalent or covalent bonding; cf. Pauling, " The Nature of the Chemical Bond," pp. 34—37, Cornell University Press, 1940]. We shall, therefore, consider the quantity $(U^{II} - 2U^{I})$ for the extreme cases, and then try to deduce its probable change in the intermediate stages.

In ionic crystals of cuprous and cupric salts with the same anions, there would be twice as many anions per cupric ion in the cupric salt as per cuprous ion, in the cuprous salt. The electrostatic energy of interaction between the bivalent ion and an anion would be twice that between the univalent ion and an anion, if the interionic distance were the same in both cases. Therefore $U^{\mathrm{II}} = 4U^{\mathrm{I}}$ (approx.). Again, for the ions in solution the simple Born expression makes the energy of solvation of a bivalent ion four times that of a univalent ion of the same radius; whence $U^{\mathrm{II}} = 4U^{\mathrm{I}}$ once more. The effective radius of Cu^{++} is less than that of Cu^{+}, and in any case the above statements are only approximate, but a survey of the hydration energies of alkali and alkaline-earth metal ions (whose hydration energies are mainly electrostatic) and the lattice energies of ionic crystals, confirms their validity as such. Thus, in the extreme ionic cases $(U^{\mathrm{II}} - 2U^{\mathrm{I}}) = 2U^{\mathrm{I}}$ (approx.). This is a fairly large negative quantity, which makes $\Delta U'$ much lower than ΔU (equation 4), and, as will be seen later, $\Delta U'$ is negative for hydrated ions and the most ionic crystals.

For almost purely covalent bonding, the quantity $(U^{\mathrm{II}} - 2U^{\mathrm{I}})$ is not so easily estimated. The energy of formation of a covalent bond does not depend directly on the charge of the ion concerned, and with some particular anion may easily be nearly the same for the two ions (cf. calculations of bond strengths given by Pauling, *op. cit.*, Chap. III). There may be at the most twice as many bonds to each cupric ion as to each cuprous ion, but it is unlikely even then that U^{II} will be greater in magnitude than $2U^{\mathrm{I}}$, and will most probably be smaller. Thus, $(U^{\mathrm{II}} - 2U^{\mathrm{I}})$ for the covalent extreme would probably be positive, but possibly only small. The general trend of $(U^{\mathrm{II}} - 2U^{\mathrm{I}})$ from ionic to covalent bonding must, therefore, be in the positive direction, and will result in a considerable increase of $\Delta U'$. The direction of change might not, however, be constant throughout the transition. The bonding in the compounds to be dealt with, and most common copper compounds, is probably either near the ionic extreme or intermediate, but still largely ionic, so the trend of $(U^{\mathrm{II}} - 2U^{\mathrm{I}})$ in this region must be considered.

The transition from ionic to covalent type is accompanied by gradual decrease of the ionic charges, and so of electrostatic interaction. Since it is the large electrostatic interaction of Cu^{++} with its surroundings, compared with that of Cu^{+}, which makes $(U^{\mathrm{II}} - 2U^{\mathrm{I}})$ a large negative quantity for the ionic extreme, it is very probable, in the region under consideration where this electrostatic interaction is decreasing but still forms a large part of the bonding energy, that $(U^{\mathrm{II}} - 2U^{\mathrm{I}})$ will decrease in magnitude as the degree of covalency increases. Hence $\Delta U'$ will change in the positive direction, *i.e.*, in the same way as its general trend throughout the transition. We may, therefore, conclude that as the polarisability of the anions or molecules interacting with the copper ions increases, so will $\Delta U'$ increase, and the cuprous compounds become more stable. It will now be shown that this conclusion is borne out by experiment. The relevant data will be, for solid compounds, the energy change $\Delta U'$ or $\Delta H'$, accompanying the decomposition reaction (2), and in the case of the reaction in solution, the equilibrium constant and ΔG° derived from it. The thermal data used in the calculations of hydration and lattice energies, etc., are from Landolt–Börnstein Tabellen, up to and including the 3rd Ergänzungsband, except where otherwise stated.

Solid Compounds.—The case of solids is conveniently dealt with first. No new data are presented, but existing data suffice to indicate the relation of the stability of cuprous compounds to the nature of the bonding.

In Table I is listed $\Delta H'$ for reaction (2) for various cuprous salts, obtained for the halides from the expression

$$\Delta H' = \Delta H + (\text{Lattice energy CuX}_2 - 2 \times \text{Lattice energy CuX})\ \text{kg.-cals.}$$

[where ΔH refers to reaction (3) and is + 207·1 kg.-cals.], and for the oxides and sulphides, from their heats of formation from the elements. The use of the lattice energies for the

TABLE I.

	Lattice energies (kg.-cals. per mol.).		
	CuX$_2$.	CuX.	$\Delta H'$.
X = F	− 727	(− 248)	(− 24)
X = Cl	− 658	− 232	+ 14
X = Br	− 645·5	− 228	+ 17·5

	Heats of formation (kg.-cals. absorbed)		
	CuX.	Cu$_2$X.	$\Delta H'$.
X = O	− 38	− 39	+ 1
X = S	− 11	− 20	+ 9

halides enables the fluorides to be included by estimating the lattice energy of cuprous fluoride by a comparison with those of the silver halides. Data for cupric fluoride are from von Wartenburg (*loc. cit.*).

In the halide group, allowance being made for the uncertainty in the case of the fluorides, the expected change of $\Delta H'$ is still clear, and the instability of cuprous fluoride and of cuprous salts of other anions of low polarisability, such as ClO_4^-, NO_3^-, SO_4^{--}, etc., may be anticipated. Von Wartenburg's demonstration of the instability of cuprous fluoride has already been mentioned. A similar change of $\Delta H'$ occurs for the oxides and sulphides, showing the greater stability of cuprous sulphide, though $\Delta H'$ for the sulphide is not as high as might be expected. It is noteworthy that $\Delta H'$ for reaction (2) in water is — 9·4 kg.-cals. (Heinerth, *Z. Elektrochem.*, 1931, **37**, 61), falling between the values for solid chlorides and fluorides; and this, despite the different conditions, corresponds with the fact that the polarisability of the water molecules is between those of chloride and fluoride ions.

Simple Ions in Water and Other Solvents.—We now consider the effect on the equilibrium (2) of using solvents in which the electrostatic interaction between the ions and solvent molecules is different from that in water. Measurements of the equilibrium concentrations (in g.-mols. or g.-ions/l.) in pure (entirely water-free) methyl and ethyl alcohols were carried out and are recorded in Table II. A solution of cupric perchlorate in the alcohol, containing perchloric acid to prevent precipitation of cuprous oxide, was brought to equilibrium with metallic copper. The temperature in all cases was 25°, and all values of free-energy changes, etc., in this section refer to this temperature.

TABLE II.

MeOH; $\varepsilon = 31{\cdot}5$.				EtOH; $\varepsilon = 24{\cdot}2$.			
($HClO_4$).	(Cu^{II}).	10^5(Cu^I).	$10^{-4}(Cu^{II})/(Cu^I)^2$.	($HClO_4$).	(Cu^{II}).	10^5(Cu^I).	$(Cu^{II})/(Cu^I)^2$.
0·081	0·0492	123	3·2	0·081	0·0304	3070	32
0·081	0·0690	119	4·8 *	0·081	0·0467	3560	37
0·081	0·0943	160	3·7	0·081	0·0705	4450	36
0·081	0·1070	178	3·3	0·081	0·1022	5540	33
				0·010	0·00159	632	40
				0·010	0·00284	825	42
				0·010	0·00459	1067	40
				0·010	0·00595	1256	38

* Unreliable, based on only one unsatisfactory analysis.

Measurements carried out by Fenwick (*J. Amer. Chem. Soc.*, 1926, **48**, 860) and Heinerth (*loc. cit.*) give as a mean value for the equilibrium constant in water at 25° $K_{H_2O} = [Cu^{II}]/[Cu^I]^2 = 1{\cdot}0 \times 10^6$ (square brackets indicate activities). Qualitatively, therefore, the expected results are obtained. With decrease of dielectric constant (ϵ) there is decrease of electrostatic interaction between the ions and the solvent molecules, whereas the covalent bonding probably remains much the same for the alcohols as for water. There is therefore a displacement of the equilibrium favouring the cuprous state.

The energies of solvation of the ions are probably very largely electrostatic even in the alcohols, and it is of interest to compare the equilibrium constants, calculated by assuming that they are entirely so, with the experimental results. The concentration ratios $(Cu^{II})/(Cu^I)^2$ must be multiplied by suitable activity coefficients, which may be done very approximately by assuming that $\gamma_{Cu^{II}}/\gamma_{Cu^I}{}^2 = \gamma_{Cu^I}{}^2$ and taking γ_{Cu^I} as 0·3 at the concentrations used (by comparison with known activity coefficients of Li^+, Na^+, K^+, in the alcohols; see Landolt–Börnstein Tabellen, Ergänzungsband III). The calculated equilibrium constants are obtained by use of the standard free energies of hydration (cf. Latimer, *Chem. Rev.*, 1936, **18**, 349; Latimer, Pitzer, and Smith, *J. Amer. Chem. Soc.*, 1938, **60**, 1829; Latimer, Pitzer, and Slansky, *J. Chem. Physics*, 1939, **7**, 108) of cupric and cuprous ions, which are found to be — 472·3 ± 1 and — 126 ± 1 kg.-cals., respectively. In the expression

$$\Delta G^\circ_{\text{alc.}} = \Delta G^\circ + (-\,472{\cdot}3 + 2 \times 126)\left\{\frac{\varepsilon_{\text{alc.}} - \varepsilon_{H_2O}}{\varepsilon_{\text{alc.}}\,(\varepsilon_{H_2O} - 1)}\right\} \text{ kg.-cals.}$$

$\Delta G^\circ_{\text{alc.}}$ and $\Delta G^\circ_{H_2O}$ refer to reaction (2) in an alcohol and in water and $\varepsilon_{\text{alc.}}$ and ε_{H_2O} are the dielectric constants of the solvents. The comparison is made in Table III. The rough agreement, in view of the approximations used, indicates that the change of electrostatic solvation energy is probably the main factor controlling the change in the equilibrium constant.

TABLE III.

	H_2O.		MeOH.		EtOH.	
	$\Delta G^\circ_{\mathrm{H_2O}}$, kg.-cals.	K.	$\Delta G^\circ_{\mathrm{MeOH}}$, kg.-cals.	K.	$\Delta G^\circ_{\mathrm{EtOH}}$, kg.-cals.	K.
Exptl.	$-8{\cdot}2$	$1{\cdot}0 \times 10^6$	$-4{\cdot}9$	4×10^3	$-0{\cdot}8$	$3{\cdot}6$
Calc.	—	—	$-3{\cdot}9$	7×10^2	$-1{\cdot}7$	18

Complex Ions in Solution.—The reactions involved in the equilibrium in aqueous solution between cuprous and cupric complex ions in presence of copper are

$$\begin{array}{lll}
2\mathrm{Cu^+X}_m = \mathrm{Cu^{++}X}_n + (2m - n)\mathrm{X} + \mathrm{Cu\ (metal)} & \Delta G^\circ_{\mathrm{X}},\ K_{\mathrm{X}} & \ldots\ 5(a) \\
2\mathrm{Cu^+\ aq.} = \mathrm{Cu^{++}\ aq.} + \mathrm{Cu\ (metal)} & \Delta G^\circ_{\mathrm{H_2O}},\ K_{\mathrm{H_2O}} & \ldots\ 5(b) \\
\mathrm{Cu^+\ aq.} + m\mathrm{X} = \mathrm{Cu^+X}_m & \Delta G^\circ_{\mathrm{I}},\ K_{\mathrm{I}} & \ldots\ 5(c) \\
\mathrm{Cu^{++}\ aq.} + n\mathrm{X} = \mathrm{Cu^{++}X}_n & \Delta G^\circ_{\mathrm{II}},\ K_{\mathrm{II}} & \ldots\ 5(d)
\end{array}$$

and the standard free-energy change and equilibrium constant are given after each. The same notation will be used later in discussing individual cases. All measurements relate to 25°. Reaction 5(*a*) refers to the decomposition of a cuprous complex ion in aqueous solution, X being the co-ordinating ion or molecule; the others are self-explanatory.

From the above it is obvious that

$$\Delta G^\circ_{\mathrm{X}} = \Delta G^\circ_{\mathrm{H_2O}} + (\Delta G^\circ_{\mathrm{II}} - 2\Delta G^\circ_{\mathrm{I}}) \quad \ldots\ldots \quad (6)$$

an expression parallel to equation (4). Here, $-\Delta G^\circ_{\mathrm{I}}$ and $-\Delta G^\circ_{\mathrm{II}}$ represent mainly the energy set free by the formation of the complex ions from the hydrated ions.

Most molecules or ions which form, with copper ions, complex ions appreciably stable in aqueous solution are more polarisable than the water molecule. In these cases, therefore, formation of the complex ion is accompanied by an increase in the covalent nature of the bonding, making $(\Delta G^\circ_{\mathrm{II}} - 2G\Delta^{c})$ a positive quantity and resulting in a displacement of the equilibrium favouring the cuprous state, greater the more polarisable the co-ordinated ion or molecule. (Fluoride, and to a less extent, sulphate, ions form, with cupric ion, complexes which are moderately stable in solution, in which the bonding must be predominantly electrostatic, but as would be expected, both from this fact and from the nature of the cuprous salts, no corresponding cuprous complexes exist in solution, if at all.)

As a measure of the displacement of the equilibrium, the ratio $[\mathrm{Cu^{++}X}_n]/[\mathrm{Cu^+X}_m]^2$ is convenient, but it depends on the concentration of X unless $2m = n$. It is related to the various equilibrium constants by the expression

$$[\mathrm{Cu^{++}X}_n]/[\mathrm{Cu^+X}_m]^2 = K_{\mathrm{X}}[\mathrm{X}]^{n-2m} = K_{\mathrm{H_2O}}[\mathrm{X}]^{n-2m}K_{\mathrm{II}}/K_{\mathrm{I}}^2 \quad \ldots \quad (7)$$

All the complex ions to be considered are stable enough for the concentration of both cuprous and cupric complexes to be taken as equal to the concentrations of cuprous and cupric copper.

The individual cases to be considered involve halogen ions and nitrogen and sulphur compounds as co-ordinating groups.

Halogen ions. The halogen ions except fluoride are more polarisable than the water molecule and will form with copper ions linkages of a more covalent character than it does. The effect increases from chloride to iodide and is particularly noticeable for cuprous ion.

Examination of an equilibrium solution containing free chloride ion, concentration = 1M approx., and $(\mathrm{Cu^I}) = 0{\cdot}20$M gave the concentration of cupric copper, $(\mathrm{Cu^{II}})$, as $0{\cdot}0042$M, so that $(\mathrm{Cu^{II}})/(\mathrm{Cu^I})^2 = 1{\cdot}0 \times 10^{-1}$. (Further measurements of these equilibria have had to be abandoned.) Work by Bodländer and Storbeck (*Z. anorg. Chem.*, 1902, **31**, 1) shows that in dilute solutions this ratio falls from 4×10^3 when $(\mathrm{Cl}^-) = 0{\cdot}0007$M to 20 when $(\mathrm{Cl}^-) = 0{\cdot}05$M. Thus, the ratio decreases rapidly with increasing chloride ion concentration (because $n < 2m$ as the ions $\mathrm{CuCl_2^-}$, $\mathrm{CuCl_3^{--}}$, and $\mathrm{CuCl_3^-}$ preponderate in these solutions), and in presence of moderate concentrations it is much lower than in water. It is very probable that comparison of equilibria would show that bromide ion stabilises the cuprous state still more than chloride, on account of its higher polarisability.

Ammonia and amines. Ammonia and most amines co-ordinate strongly with both ions of copper. Examination of equilibrium solutions containing ammonia gave the results shown in Table IV. Cols. 2—4 show the amounts of copper sulphate, sulphuric acid, and ammonia, expressed as ml. of M-solution, used in making up 100 ml. of each original solution, which was then brought to equilibrium with metallic copper. The sulphuric acid was included to provide an ammonium-ion concentration sufficient to inhibit almost entirely the reaction $\mathrm{NH_3 + H_2O \longrightarrow NH_4^+ + OH^-}$. To get measurable amounts of cupric copper, fairly concentrated solutions had to be used. Activities will be considerably different from concentrations, but use of the ratio $(\mathrm{Cu^{II}})/(\mathrm{Cu^{I}})^2$ instead of the ratio of activities will not obscure large-scale changes, and where small-scale variations are under consideration, constant ionic strengths have been used.

TABLE IV.

Ammonia. Temperature 25°.

No.	M-$\mathrm{CuSO_4}$, ml.	M-$\mathrm{H_2SO_4}$, ml.	M-$\mathrm{NH_3}$, ml.	Total $\mathrm{SO_4^{--}}$ concn., M.	$(\mathrm{Cu^{II}})$, M.	$(\mathrm{Cu^{I}})$, M.	$\frac{(\mathrm{Cu^{II}})}{(\mathrm{Cu^{I}})^2} \times 100$.	Excess $\mathrm{NH_3}$ concn., M.
1	5	30	120	0·35	0·00047	0·100	4·6	0·4
2	15	20	190	0·35	0·00236	0·297	2·7	0·9
3	10	60	230	0·70	0·00092	0·203	2·23	1·3
4	30	40	380	0·70	0·00961	0·601	2·67	1·8
5	30	20	200	0·50	0·00602	0·581	1·78	0·42
6	30	20	304	0·50	0·00654	0·580	1·94	1·45
7	30	20	304	0·50	0·00669	0·580	1·99	1·45
8	30	20	360	0·50	0·00741	0·575	2·26	2·02
9	30	20	480	0·50	0·00965	0·573	2·94	3·22
10	30	20	480	0·50	0·00869	0·572	2·66	3·22

In solutions containing excess ammonia it is well known that the cupric ion is present almost exclusively as $\mathrm{Cu(NH_3)_4^{++}}$ (see, *e.g.*, Job, *Ann. Chim.*, 1927, **9**, 113). Hence, $n = 4$, and the slight change in the ratio $(\mathrm{Cu^{II}})/(\mathrm{Cu^{I}})^2$ with change in the concentration of free ammonia (in Nos. 5—10, Table IV) shows that $m = 2$ very nearly. Calculation from these figures by using equation (7) gives $m = 1{\cdot}9$. Probably the cuprous copper is present almost entirely as $\mathrm{Cu(NH_3)_2^+}$ and the change in the ratio is due to the change in the nature of the solvent as $(\mathrm{NH_3})$ increases. This is in agreement with the existence of such salts as $\mathrm{[Cu(NH_3)_2]NO_3}$ and $\mathrm{[Cu(NH_3)_2]_2SO_4}$ and with the work of Bjerrum (*K. dansk. Vidensk. Selsk. mat.-fys. Medd.*, 1934, **12**, No. 15).

The average value of $K_{\mathrm{NH_3}}$ being taken as 2×10^{-2}, $\Delta G_{\mathrm{NH_3}}$ is found to be $+\ 2{\cdot}3$ kg.-cals. for the reaction $\mathrm{2Cu(NH_3)_2^+ \longrightarrow Cu(NH_3)_4^{++} + Cu}$ (metal) in water, compared with $\Delta G_{\mathrm{H_2O}} = -\ 8{\cdot}2$ kg.-cals. for the reaction involving hydrated ions. The difference, $+\ 10{\cdot}5$ kg.-cals., represents $(\Delta G^{\circ}_{\mathrm{II}} - 2\Delta G^{\circ}_{\mathrm{I}})$ (equation 6) and is the source of the increased stability of the cuprous state. Since there are only two $\mathrm{NH_3}$ molecules attached to the cuprous ion, and four to the cupric ion, the positive value of $(\Delta G^{\circ}_{\mathrm{II}} - 2\Delta G^{\circ})$ is probably due rather to decrease in the total electrostatic interaction than to the increase in the covalent bonding.

Methylamine and pyridine. Methylamine being a stronger base than ammonia, smaller concentrations of copper salts had to be used to prevent precipitation of cuprous oxide on the copper. The amount of cupric copper present was then too small for accurate measurement, but the methylamine appeared to favour the cuprous state even more than ammonia. In the presence of pyridine, the equilibrium was similar, but the pyridine interfered with the method of titration, so analyses could not be carried out.

Diamines. The stabilisation of the cuprous state with respect to the cupric state and copper by monoamines appears to be a general phenomenon, as would be expected.

Ethylenediamine, however, has a considerable power of stabilising the cupric state in solid salts and in solution (*e.g.*, the bisethylenediaminocupric ion is not even reduced by hypophosphite ion but forms a stable salt with it). The equilibrium in presence of ethylenediamine was therefore investigated, and the results are recorded in Table V (constructed similarly to Table IV). The actual values of the ratio are obviously inaccurate owing to the smallness of (Cu^I) and the difficulty of determining it accurately (see p. 811) (the true values of the ratio are probably higher than those given), but there is undoubtedly a large difference from the behaviour of a monoamine. Further, it is noteworthy that addition of ethylenediamine to cuprous chloride dissolved in potassium chloride solution, in absence of air, caused immediate precipitation of copper, and formation of bisethylenediaminocupric ion.

TABLE V.

Ethylenediamine. Temperature 25°.

M-$CuSO_4$, ml.	M-H_2SO_4, ml.	M-$C_2H_8N_2$, ml.	Total SO_4^{--} concn., M.	(Cu^{II}), M.	(Cu^I), M.	$\frac{(Cu^{II})}{(Cu^I)^2} \times 10^{-5}$.	Excess $C_2H_8N_2$, M.
5	15	45	0·20	0·0501	0·00071	0·9	0·20
10	10	50	0·20	0·0982	0·00105	1·0	0·20
10	10	60	0·20	0·0981	0·00048	4·4	0·30
10	10	70	0·20	0·0996	0·00062	2·5	0·40

In order to study the reasons for this difference of behaviour between mono- and di-amines, equilibria in presence of other diamines were investigated. Results for tri- and penta-methylenediamines are shown in Table VI. The cupric state is favoured somewhat less by trimethylenediamine than by ethylenediamine, though both these substances form chelate complexes with the cupric ion (for trimethylenediamine, see Werner, *Annalen*, 1912, **386**, 264). When the two amino-groups are separated by five carbon atoms, as in pentamethylenediamine, chelation probably does not occur, only one amino-group of each molecule is bonded to the cupric ion, and the ratio $(Cu^{II})/(Cu^I)^2$ is approximately the same as in the presence of a monoamine.

TABLE VI.

	M-$CuSO_4$, ml.	M-H_2SO_4, ml.	M-Diamine, ml.	Total SO_4^{--} concn., M.	(Cu^{II}), M.	(Cu^I), M.	$\frac{(Cu^{II})}{(Cu^I)^2}$.	Excess diamine, M.
$C_3H_6(NH_2)_2$	10	10	26	0·20	0·0980	0·00140	$5·0 \times 10^4$	0·06
	15	5	36	0·20	0·1467	0·00152	$6·3 \times 10^4$	0·06
	5	15	30	0·20	0·0486	0·00220	$1·0 \times 10^4$	0·20
	10	10	40	0·20	0·0967	0·00268	$1·3 \times 10^4$	0·20
	10	10	70	0·20	0·0948	0·00794	$1·5 \times 10^3$	0·40
	2	18	52	0·20	0·0196	0·0014	$1·0 \times 10^3$	0·30
$C_5H_{10}(NH_2)_2$	2	18	52	0·20	0·00005	0·040	3×10^{-2}	0·30

Since the cuprous ion in solution seems able to take up only two molecules of ammonia (see p. 807), and since the bonds employed are probably at an angle of 180° (cf. Pauling, *op. cit.*, p. 89), it is understandable that if this ion forms chelate complexes with ethylene- and trimethylene-diamines at all, the bond energies will be low, and it may, in preference, attach two diamine molecules each by one amino-group. [The change of $(Cu^{II})/(Cu^I)^2$ with change of trimethylenediamine concentration corresponds roughly to $(n - 2m) = -2$, *i.e.*, $m = 2$.] The stability of the cupric chelate rings, the five-membered one derived from ethylenediamine being rather more stable than the six-membered one from trimethylenediamine, would then explain why these diamines stabilise the cupric rather than the cuprous state.

Sulphur compounds. The sulphur atom is more polarisable than the nitrogen atom, indicating still more covalent bonding and a further stabilisation of the cuprous state. This is certainly the case, since both methyl sulphide and ethylenethiourea give stable derivatives of cuprous salts, not of cupric, when added to a solution of a cupric salt (Phillips, *J. Amer. Chem. Soc.*, 1901, **23**, 25; Morgan and Burstall, J., 1928, **143**). Many other sulphur compounds behave similarly. By analogy with ethylenediamine, a disulphide such as αβ-di(methylthio)ethane, $CH_3{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_3$ might be expected to show some preferential co-ordination on to the cupric ion. An alcoholic solution of this compound added to alcoholic cupric perchlorate solution gave an immediate brown precipitate, presumably the perchlorate of the cupric complex ion. A similar precipitate is formed in aqueous solution on shaking (the disulphide is very sparingly soluble). On adding excess of the disulphide to aqueous copper sulphate solution, a green colour developed which disappeared on equilibration with copper, leaving a colourless solution in which no cupric compound was detectable. The copper lost in weight an amount equivalent to the original cupric salt. Hence, the only evidence for any preferential co-ordination of such disulphides on to the cupric ion is their ability to give fairly stable compounds with cupric salts, *e.g.*, the brown compound mentioned above and others with cupric chloride (Morgan and Ledbury, J., 1922, **121**, 2882; Tschugaev, *Ber.*, 1908, **41**, 2226), which, as mentioned by Tschugaev, does not seem possible for monosulphides. Though this may be so, the degree of covalent bonding is sufficient to cause the equilibrium solution even in presence of the disulphide to contain no detectable cupric compound.

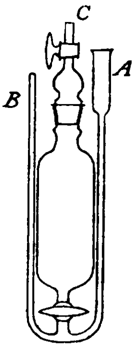
The conclusions may be summarised as follows: The reaction $2Cu^+ \longrightarrow Cu^{++} + Cu$ (metal) involving ions in the gas phase is accompanied by a large absorption of energy. In crystals and solutions, in which the interaction of the copper ions with their surroundings is mainly electrostatic, the interaction energy of the cupric ion is sufficiently greater than that of two cuprous ions to reduce this to a small absorption, or even an evolution of energy. This permits the easy decomposition of these cuprous salts. As the bonding becomes less electrostatic and more covalent, the energy absorption increases again and the cuprous compounds are stabilised, except in such special cases as the complexes with the lower diamines.

EXPERIMENTAL.

The general principle of the method used for measuring the equilibrium concentrations was as follows. A solution containing the cupric salt was made up in a specially constructed vessel, a piece of pure copper foil added, and the vessel rotated in a thermostat at 25° for several days. The solution was then removed (out of contact with air), and the concentrations of cupric and cuprous copper estimated.

Reagents.—" AnalaR " Copper sulphate containing no detectable iron or chloride was crystallised once and used for preparing an approximately 1M-solution, the concentration of which was determined by addition of iodide and titration by thiosulphate. The copper foil was specially pure (electrolytic) foil supplied by B.D.H. Other substances were tested and purified when necessary by the usual methods. Trimethylene- and pentamethylene-diamines were prepared by the Gabriel synthesis, and αβ-di(methylthio)ethane was obtained pure by the methods of Morgan and Ledbury (*loc. cit.*).

Preparation of Equilibrium Solutions.—The equilibrating vessel is shown in the figure. The body is cylindrical, of capacity about 200 ml., and it is fitted with a ground-in stopper (*C*). This carries a tap as shown, through which a pressure of nitrogen can be applied to expel the solution through the exit tube at the bottom.



The vessel was filled, in the case of aqueous solutions, by introducing measured volumes of the required solutions and sufficient water to make 100 ml. To displace all oxygen, a stream of oxygen-free nitrogen was passed through the liquid *via* tube *B*, tube *A* being closed by a rubber bung, and tap *C* open. The ammonia was added last, after nitrogen had been passing for some time, to avoid unnecessary loss by volatilisation. A roll of cleaned copper foil was then quickly introduced, the stopper replaced, and, after passage of nitrogen for a further ½ minute or so, both taps were closed. Tube *B* was then closed, stopper *C* fixed in position by rubber bands, and the vessel transferred to the thermostat at 25·00° ± 0·05° for equilibration. Trial showed that four days was ample time for the attainment of equilibrium.

At the end of this time, the vessel was clamped in an upright position in the thermostat, tube *B* and the one on the stopper *C* connected to the nitrogen supply, and into *A* a rubber bung fitted, carrying a tube connecting by a ground glass joint to a burette with a three-way tap. A plug of glass wool with some Gooch asbestos was inserted in the enlarged end of tube *A* before the rubber bung, to filter out any particles of copper. By an arrangement of T-pieces and taps, the air could be completely displaced from the burette and the rest of the apparatus by nitrogen (escaping gas tested for absence of oxygen by alkaline pyrogallol), and finally, the solution was transferred (by the nitrogen pressure) to the burette and run out for analysis.

For solutions in absolute methyl and ethyl alcohols, special methods had to be used. Copper sulphate is not appreciably soluble in these alcohols, and copper perchlorate, which is, could be dehydrated in a vacuum at 100° to $Cu(ClO_4)_2,2H_2O$, but no further, without decomposition (loss of acid). Moreover, anhydrous perchloric acid cannot be safely added to absolute alcohols. Therefore, the alcohol, after dehydration by magnesium, was distilled directly into a vessel containing a roughly weighed quantity of anhydrous silver perchlorate in an atmosphere of air dried by phosphoric oxide. Dried hydrogen chloride equivalent to only a part of the silver salt (from a weighed quantity of pure ammonium chloride acted upon by concentrated sulphuric acid) was passed into the solution with a stream of dry air. Silver chloride was precipitated, its solubility in these alcohols being less than in water. The vessel was also connected *via* a sintered-glass filter to an equilibrating vessel containing a roll of copper foil. After displacement of all oxygen from the apparatus and the solution by a stream of pure dry nitrogen, the solution was forced by the nitrogen pressure through the sintered-glass filter into the equilibrating vessel. The solution, containing perchloric acid and silver perchlorate (but no water), reacted with the copper during the equilibration, giving finally an equilibrium mixture of cuprous and cupric perchlorates and a precipitate of silver. [The known standard electrode potentials of copper and silver in methyl alcohol show that the concentration of silver ion remaining in solution will be negligible. The same, it may be said with confidence, will apply to the ethyl-alcoholic solution.] The coating of silver formed on the copper peeled off after a time, leaving a clean copper surface.

Analysis of Solutions.—Fenwick and Heinerth (*locc. cit.*) both used electrometric titrations, with permanganate or ceric sulphate, for the estimation of cuprous copper. These methods were found, as expected, to be unsatisfactory in the presence of amines or alcohols. The method used, and found to be satisfactory in all cases except in presence of pyridine, was the iodine–thiosulphate method for copper with some modifications. The thiosulphate was standardised against pure copper.

To carry out a titration, the requisite excess of recrystallised potassium iodide was dissolved in water in a conical flask and acidified with slightly more acetic or sulphuric acid than sufficient to neutralise the amine or ammonia (if present) in the copper solution to be used. If a trace of iodine colour appeared, it was removed by one or, at the most, two drops of N/100-thiosulphate. Air was displaced by a stream of air-free carbon dioxide passed through the solution for 10 minutes, and then, after stopping the flow (to avoid loss of iodine) but retaining the atmosphere of carbon dioxide, a volume of the copper solution was run in under the surface of the liquid from the extended jet of the burette, with gentle shaking.

The cuprous copper is, in this way, all precipitated as the iodide with no liberation of iodine, and the cupric copper is similarly precipitated but with liberation of iodine. This iodine was titrated with thiosulphate, 2—3 g. of potassium thiocyanate, without which accurate titration would be impossible (cf. Foote and Vance, *J. Amer. Chem. Soc.*, 1935, **57**, 845), being added after the starch. Although in presence of much precipitate the final colour change is from fawn to white, the end-point could be obtained accurately to within 3 drops of N/100-thiosulphate. The cupric copper having thus been estimated, ammonia was added to the liquid, which was then allowed to stand (with occasional stirring) till atmospheric oxidation caused the cuprous iodide to dissolve to a blue solution. The total copper was then precipitated by passing in hydrogen sulphide, the sulphide filtered off in a sintered-glass crucible, dissolved in 20% nitric acid on the water-bath, the sulphur filtered off, and after removal of the nitrous acid by addition of urea, the total copper was estimated (in an aliquot part, if necessary) by thiosulphate as before.

The detailed procedure differed according to whether the solution contained (1) mainly the cuprous compound, (2) mainly the cupric compound, or (3) both in similar concentration. (1) In the first case (as in the presence of ammonia, etc.) the iodine liberated by the cupric copper was titrated with approx. N/100-thiosulphate and the total copper estimated by approx. N/10-thiosulphate.

(2) In these circumstances, the iodine liberated by the cupric copper was titrated almost to the end-point with approx. N/10-thiosulphate, titration being completed with the approx. N/100-thiosulphate. In determining the total copper the same volume of the same N/10-thiosulphate solution was run in from the same section of the same burette (the volume thus obtained being reproducible to within 0·01 ml. as shown by weighing), and the titration was completed as before with the N/100-thiosulphate. The possible error is, of course, at least

0·1 ml. of the N/100-thiosulphate. This procedure is necessary because the small proportion of cuprous copper is determined by difference between the relatively large amounts of total and cupric copper. For instance, in the most dilute solution in methyl alcohol, duplicate analyses gave (Cu^{II}) = 0·0494, 0·0493M, and (Cu^{I}) = 0·00141, 0·00116M, but in all other cases, except in some with ethylenediamine solutions, the agreement was much better.

(3) When the concentrations of cupric and cuprous copper were similar, as in the ethyl-alcoholic solutions, straightforward titrations with either N/10- or N/100-thiosulphate were possible for both the cupric and the total copper, and good agreement between results of different analyses was easily obtained.

The author thanks Mr. D. C. M. Moores for his valuable assistance in the experimental work.

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[*Received, September 1st,* 1941.]