The Computation of Pourbaix Diagrams

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Pourbaix diagrams illustrate graphically the dominant solution or precipitate species of a component or components as a function of pH and oxidation potential (1). They are particularly useful for defining the conditions for selective precipitation or solution in hydrometallurgical extraction (2) and for passivation of metals. However, they are tedious to produce manually, especially when a number of components are present. The purpose of this paper is to demonstrate the principles of automatic computation for simple and complex systems and to illustrate these by reference to the copper and sulphur systems both separately and combined. The same methods are applied to the delineation of the conditions under which various chloride complexes of copper will predominate as a function of chloride activity rather than pH.

Principles

Figure 1 shows a Pourbaix diagram for sulphur compounds in water. The point of the diagram is to indicate which compound of sulphur has the highest activity at combinations of pH and oxidation potential. It shows for example that in oxidising, alkaline solutions the sulphate ion dominates, whereas in reducing, acid solutions aqueous hydrogen sulphide is the major sulphur compound. In acid conditions of intermediate oxidation potential a wedge-shaped region is found which defines the circumstances under which precipitation of sulphur can occur.

An odd feature of the diagrams, as described here, is that unless the solution compounds have equal and constant activity coefficients, the concentrations of these compounds in their respective zones are not equal and could in principle be very different. To remove this anomaly the activity coefficients could readily be incorporated provided they were independent of pH and pE, the variables of the system.

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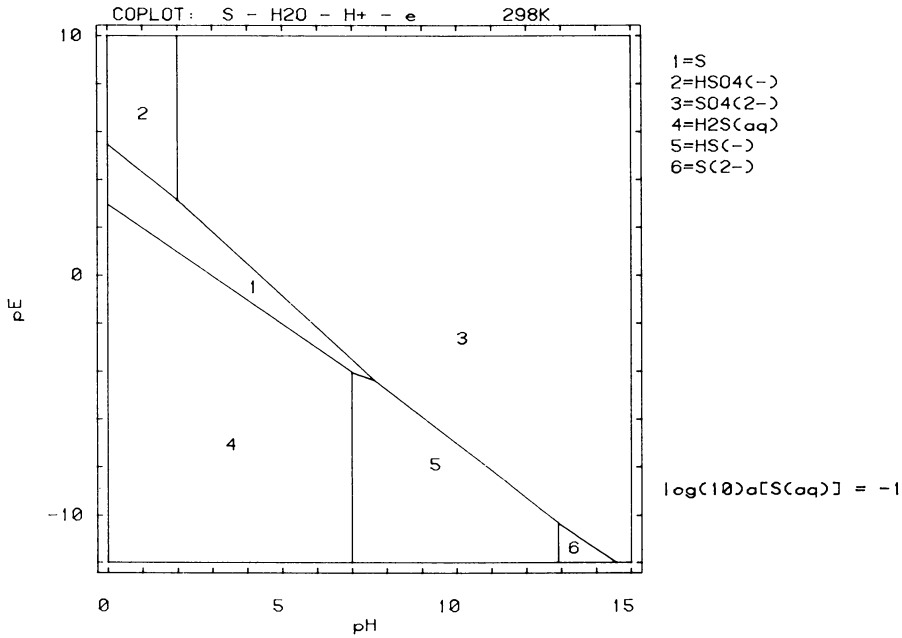

Figure 1. A pH–pE diagram for the S–H_2O–H^+–e system at 298.15 K. The activities of the predominant sulphur compounds in solution are 10^{-1}.

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The diagrams calculated by the methods described differ to some extent from many available in the literature in that they omit the predominant solution compound in areas where a condensed compound also forms. This greatly simplifies the diagrams without impairing their usefulness for most purposes.

The system defined by figure 1 has four components, $S - H_2O - H^+ - e$. It is important to note that these fall into two classes. Sulphur will be classified as a type 1 component to signify that we are interested in what compounds it forms. Condensed type 1 compounds, have an activity of 1 if present and > 1 if absent. The activities of the predominant type 1 compounds in solution can be fixed at any desired value. In figure 1 they are set at 10^{-1}. Thus the sulphate ion has an activity of 10^{-1} in its area and HS^- has an activity of 10^{-1} in its area. On the line between these areas HS^- and the sulphate ion coexist with equal activities and the position of the coexistence line between these two compounds can be obtained by solution of the equation for the equilibrium

$$SO_4^{2-} = HS^- + 4H_2O - 9H^+ - 8e.$$

The remainder of the components are of type 2. Their activities are either fixed, as for H_2O, or they form the independent variables of the system, H^+ and e. The activities of H^+ and the notional activity of the electron are expressed in logarithmic form as pH and pE where pE is related to the oxidation potential, E_h, by the relation

$$E_h = \frac{RT \ln 10}{F} pE \qquad 1$$

There are 6 sulphur compounds to be considered and therefore 15 possible coexistence lines of which only 9 represent stable equilibria. Moreover, even these 9 lines are valid (i.e. correspond to stable coexistence) along only part of their possible extents. The problem then is to determine the equations for the lines and the range over which they are valid, and to provide a method for plotting them.

Methods for a simple case

The principles of the method become much clearer if applied to a particular rather than the general case.

1 The first step is to list the compounds of the type 1 component together with their Gibbs energies of formation at the chosen temperature, or the function $[\Delta H^\circ(f, 298) + G^\circ(T) - H^\circ(298)]$ which is much easier to calculate in a data-bank. The two functions must not be used for different substances in the same calculation.

The data used in this paper are taken from the monograph by Duby (3) on aqueous systems of copper.

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Table I

No.	Compound Formula	$\Delta_f G^\circ$ (298) /kJ mole^{-1}
1	S	0
2	HSO_4^-	-756.01
3	SO_4^{2-}	-744.63
4	H_2S(aq)	-27.87
5	HS^-	12.05
6	S^{2-}	85.77

This is not a complete list of type 1 compounds in the system but it is sufficient to demonstrate the principles. In this table, the formulae of the compounds are just as essential items of data as the Gibbs energies, since, as will be seen, they are used to generate the stoichiometry numbers in the equations for reactions.

2 The next stage is to choose a reference compound of the type 1 component. Unless it is very far from stable in the system, it is advantageous to choose the element, rhombic sulphur in this case.

3 Equations are then written for the conversion of one mole of the reference compound to all other compounds of the type 1 component using the type 2 components to balance the equations.

$$1,2 \quad S = HSO_4^- - 4H_2O + 7H^+ + 6e$$

$$1,3 \quad S = SO_4^{2-} - 4H_2O + 8H^+ + 6e$$

$$1,4 \quad S = H_2S(aq) - 2H^+ - 2e$$

$$1,5 \quad S = HS^- - H^+ - 2e$$

$$1,6 \quad S = S^{2-} - 2e$$

The numbers to the left of the equation identify the compounds of sulphur participating in each equation. Note that any other equation can be generated by subtraction of pairs of these equations. Thus equation 3,5 is generated by subtracting equation 1,3 from equation 1,5. The order is important.

$$3,5 \quad SO_4^{2-} = HS^- + 4H_2O - 9H^+ - 8e$$

4 The standard Gibbs energy changes for the reactions of the reference compound are then calculated. They are listed in column 2 of table 2.

Non-standard Gibbs energy changes can be calculated from the following equation.

$$\Delta G = \Delta G^\circ + RT \sum_{g=1}^{m+1} \nu_g \ln a_g \qquad 2$$

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where g defines the position of the compounds in the equation and m is the number of components. For the system S - H_2O - H^+ - e, there are 4 components and, therefore, 5 compounds in each equation. The stoichiometry number for compound g in the equation is given the symbol ν_g, which may be zero. The stoichiometry number for the reference compound is always -1, as it always lies on the left of the equation and is always assigned 1 mole.

For a given diagram the activity of the sulphur solution species can be set to any desired value. The activity of elemental sulphur and water are both unity. The logarithms of the activities of the hydrogen ion and the electron are for convenience assigned the symbols X and Y respectively. Thus X = -pH and Y = -pE. For the particular case of reaction 1,3 the following equation is obtained for $\Delta G/R'T$ where R' = R ln 10

$$-\frac{\Delta G}{R'T} = \left(-\frac{\Delta G^{o}}{R'T} - \log a_2\right) - 8X - 6Y \qquad 3$$

where a_2 is the predetermined activity of the sulphur compounds in solution. Log a_1 = 0 and is therefore omitted.

In the general case it is convenient to assign the symbol ψ to the bracketed term where

$$\psi = -\frac{\Delta G^{o}}{R'T} - \sum_{g}^{m-1} \nu_g \log a_g \qquad 4$$

and where the summation now omits the variables of the diagram to be calculated.

When it is remembered that $-\Delta G^{o}/R'T = \log K$ it can be seen that ψ has the nature of log K adjusted for the activities of the fixed components.

Equation 2 can now be rewritten

$$\chi = \psi - \alpha X - \beta Y \qquad 5$$

where α and β are stoichiometry coefficients for the independently variable components and where

$$\chi = -\Delta G/R'T \qquad 6$$

At equilibrium χ = 0 and lines of coexistence between the compounds of the type 1 component have the algebraic form

$$\psi - \alpha X - \beta Y = 0 \quad \text{(equilibrium condition)} \qquad 7$$

Stage 4 is completed by making a table of values of ψ, α and β for the chemical equations 1,2 to 1,6. If the maximum activity of the solution compounds of sulphur is set at 10^{-1}, the following table is obtained:

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Table II

Parameters for the S-H_2O system

Equation Number	ΔG^o/kJ mole^{-1}	log K	ψ	α	β
1,2	192.707	-33.763	-32.763	7	6
1,3	204.087	-35.757	-34.757	8	6
1,4	-27.87	4.882	5.882	-2	-2
1,5	12.050	-2.111	-1.111	-1	-2
1,6	85.772	-15.027	-14.027	0	-2

The last three columns of table 2 form the basic set of input data for further calculation. Values of ψ, α and β for any other reaction can readily be obtained by subtraction as follows

$$\psi(ij) = \psi(1j) - \psi(1i)$$
$$\alpha(ij) = \alpha(1j) - \alpha(1i) \text{ etc} \qquad 8$$

Thus only the data for reactions of the reference compound need to occupy space in the computer core.

5 Key features of Pourbaix diagrams are the points of intersection between the coexistence lines. In a simple diagram, three compounds of a dependent component can coexist at these points. Thus, if compounds i, j and k coexist at a point, 3 coexistence lines must radiate from the point, ij, jk and ik. The coordinates of potential triple intersection points can be determined by simultaneous solution of pairs of equations. For example the coordinates of the equilibrium point between sulphur, SO_4^{2-} and HS^- are determined by solution of the equations

$$1,3 \quad -34.757 - 8X - 6Y = 0$$
$$1,5 \quad -1.111 + X + 2Y = 0$$
$$X(1,3,5) = -7.618 \text{ , pH } = 7.618$$
$$Y(1,3,5) = 4.3645, \text{ pE} = -4.3645$$

6 The next step is to determine whether the calculated points are valid or not. The simplest test is to determine which reactions for formation of the sulphur compounds have the highest values of χ, i.e. the lowest (most negative) ΔG. If a potential intersection point, X(ijk), Y(ijk) is valid then the values of $\chi(1,i)$, $\chi(1,j)$ and $\chi(1,k)$ should fulfil three criteria. They should be higher than any other value of $\chi(1,g)$, greater than or equal to zero and equal to each other except for rounding off errors.

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Referring to table 2 it is found that for X = -7.618, Y = 4.3645

$\chi(1,2) = -5.624$

$\chi(1,3) = 0$

$\chi(1,4) = -0.625$

$\chi(1,5) = 0$

$\chi(1,6) = -5.298$

Note that $\chi(1,1)$ need not be calculated as it is always zero. The results show the triple intersection is valid because $\chi(1,1)$, $\chi(1,3)$ and $\chi(1,5)$ are higher than the remaining values of χ. Thus coexistence lines 1,3, 1,5 and 3,5 do indeed radiate from pH = 7.618, pE = -4.3645. Valid intersection points are stored together with values of i, j and k.

7 For the purpose of computer calculation potential coexistence lines fall into a number of classes.

a they are nowhere valid (other compounds are always more stable).

b They are valid only outside the boundaries of the diagram.

c They make two valid intersections with the diagram boundaries but make no intersections within it.

d They make one valid intersection with the diagram boundary and one valid intersection within the diagram.

e They make two valid intersections within the diagram.

Intersections with the diagram boundary must therefore be calculated for each potential line and tested for validity in an analogous way to the triple intersections. Once two valid intersections of either kind have been found for a line it need not be reconsidered.

For simplicity intersections between pairs of lines ij and jk can be taken in numerical order, evaluating X(ijk) and Y(ijk) with $i < j < k$ and $k \leq n$, where n is the number of compounds. The maximum number of intersection points that need to be examined is $\binom{n}{3}$, i.e. $n(n-1)(n-2)/6$. For 40 compounds it is 9880. This is not a very large number for a computer to handle because the actual calculations are very trivial. Nevertheless, methods are available for improving the programme efficiency as briefly described under program comparisons.

It should explicitly be stated at this point that it is not possible, except by accidental coincidence, for an intersection between two lines i,j and k,l to be valid if either i or j is not equal to either k or l. Thus such intersections need never be considered.

The coordinates of the two valid intersection points for each real line can be stored in an array. When all intersections have been calculated, this array constitutes the output file to the plotter, which should be programmed to draw straight lines between the coordinate pairs corresponding to a given line. It is useful

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to note that the lines themselves do not need to be identified in the output to the plotter. All that is necessary is to have a method for labelling the areas they enclose.

The following method can be used to label the areas in which the compounds predominate. The X and Y coordinates respectively are summed for the corners of the areas occupied on the diagram by each compound in turn, including the diagram corners if the compound is stable there. The average values of X and Y are used to centre the label. A flag can be assigned to any compound that is nowhere predominant, so that its label can be omitted from the diagram.

The methods described above were used to produce figure 1 for the $S - H_2O$ system and figure 2 for the $Cu - H_2O$ system. In common with practical experience, figure 2 shows there is no combination of pH and oxidation potential for which the cuprous ion is the dominant compound of copper.

Methods for more complex diagrams

Up to this point the paper has been concerned only with simple diagrams for which there is only one type 1 component. If more than one type 1 component is present each area of the diagram corresponds in general to as many compounds as there are type 1 components. Moreover, if the type 1 components form compounds between each other, in this case Cu_2S and CuS, it is necessary to fix from the start the proportions of the type 1 components. Logically, the proportions should correspond with the values set for the solution concentrations. Thus, if the concentration of sulphur in solution greatly exceeds that of copper, each area will correspond to one copper compound, which may also be a compound of sulphur, and one sulphur compound which is not also a compound of copper.

Ideally a computer system for calculation of Pourbaix diagrams would comprise a database for a wide range of compounds coupled to a computer program that would undertake the following tasks.

1 Upon input of the system expressed as components the computer would retrieve data for compounds of the type 1 components with each other and with the type 2 components. Data are given in table 4.

If variables other than pH and pE are to be used as coordinates of the diagram, they must be specified, together with any other type 2 components, so that data can be retrieved.

2 The type 1 compounds would be sorted into lists. For example, if the proportion of sulphur substantially exceeded that of copper, the lists would comprise

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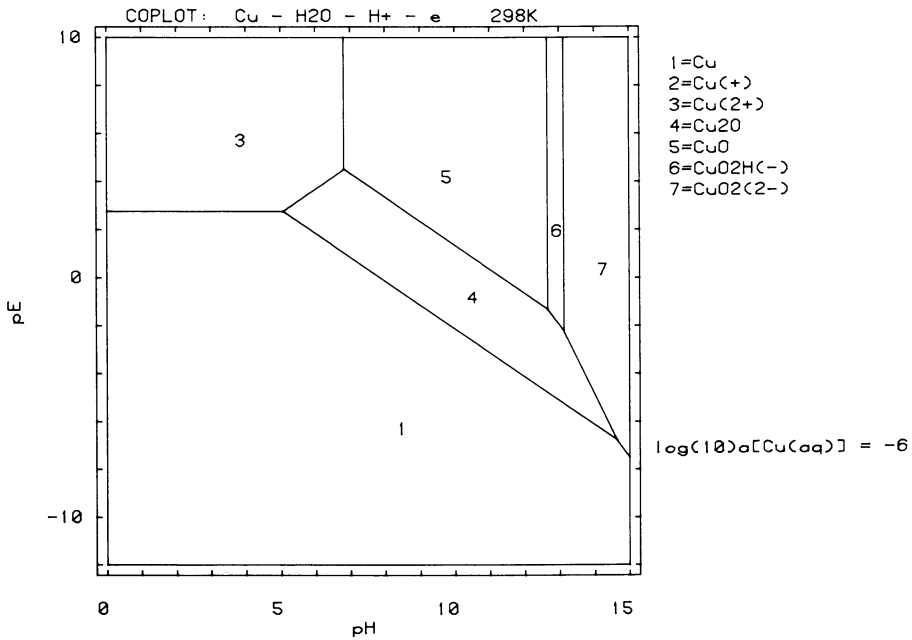

Figure 2. A pH–pE diagram for the Cu–H_2O–H^+–e system at 298.15 K. The activities of the predominant copper compounds in solution are 10^{-6}.

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	Copper Compounds			Sulphur Compounds	
1	Cu	6	CuO_2H^-	1	S
2	Cu^+	7	CuO_2^{2-}	2	HSO_4^-
3	Cu^{2+}	8	Cu_2S	3	SO_4^{2-}
4	Cu_2O	9	CuS	4	H_2S
5	CuO			5	HS^-
				6	S^{2-}

If, on the other hand the diagram were required for the case where the proportion of copper exceeded that of sulphur, Cu_2S and CuS would occur in the sulphur rather than the copper list.

3 Equations would be written in matrix form for formation of all possible combinations of type 1 compounds selected one at a time from each list, using as reference the elements or compounds in proportions adequate to ensure that the dominant type 1 component is always present independently. In the chosen example sulphur is the dominant component and an S:Cu ratio of 2:1 is adequate for this purpose. Equations can readily be calculated by matrix algebra for all possible reactions of the reference compounds. Eg

$$(CuS + S) = 0.5Cu_2S + 1.5SO_4^{2-} - 6H_2O + 12H^+ + 9e$$

$$(CuS + S) = 0.5Cu_2S + 1.5HS^- - 1.5H^+ - 3e$$

Note that (CuS + S) is used as the reference state rather than (Cu + 2S) because it is the combination of lower Gibbs energy. The combination (CuS + S) is treated as a single compound in the programs used at NPL with a stoichiometry number of -1 as it is on the left of the equation.

The computer would store the stoichiometry numbers in an array. Because the number of combinations may in some cases be large, it may be desirable to eliminate incompatible combinations such as $H_2S(aq) + CuO_2^{2-}$ either manually or automatically on the basis of previously calculated diagrams for the individual systems.

4 For each equation values of ψ, α and β calculated. If the same values of α and β are found for more than one equation, only the equation corresponding to the highest value of ψ is selected for reasons given in the following section.

5 The intersection points between coexistence lines and of coexistence lines with the boundaries of the diagram are calculated in the same way as already described for simple diagrams. However, in systems of more than one type 1 component quadruple intersections can occur at which for example HSO_4^-, SO_4^{2-}, Cu^{2+} and Cu_2S coexist. In such a case four values of χ will be found to be equal at the intersection point showing that it is the

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intersection point of four lines.

The resultant diagram is shown in figure 3. The correspondence with figure 1 can readily be seen but the stability of the copper sulphides results in great differences from figure 2. The sharp changes in direction of the boundaries of the regions where the sulphides of copper predominate show how marked are the effects of change of ionic state of the sulphur. The sulphides are stable only at intermediate oxidation potentials.

If copper rather than sulphur had been made the dominant type 1 component the $Cu - H_2O$ diagram would form part of the diagram and it would be overlain by a region in which Cu_2S was also present. Neither CuS nor S would appear on the diagram.

Variations of Pourbaix diagrams

The chief limitation of Pourbaix diagrams is that they show only the dominant compound in any particular area. They do not show the presence of other compounds, which may be of comparable concentration nor the fact that the activities of solution species are continuous functions.

A particular problem is found for systems in which a complexing agent such as Cl^- or NH_3 is present. In such cases a number of different complexes may be found for the same valence state of the cation. Because the valence state is constant these must be represented on a Pourbaix diagram only by the dominant complex. Even excluding partly hydrolysed complexes (by selecting acid conditions), there are at least 11 ionic forms of Cu^+ and Cu^{2+}

Cu^+	$CuCl_3^{2-}$	$CuCl_2$ aqueous
CuCl solid	Cu^{2+}	$CuCl_3^-$
CuCl aqueous	$CuCl^+$	$CuCl_4^{2-}$
$CuCl_2^-$	$CuCl_2$ solid	

It would be possible to consider chloride as a type 1 component in this system so that the diagram could reveal areas in which Cl_2(gas), Cl^-, ClO_3^- and ClO_4^- predominated. However, to do so here would obscure the question of how to deal with the various chloride complexes of cuprous and cupric ions, which is the principle concern of this section.

The equations for the formation of all chloride complexes of Cu^{2+} differ only in the number of Cl^- ions necessary to balance the equations. The stoichiometry numbers, α for H^+ and β for the electron are all zero and two respectively, as shown in table 3. A method for selecting the dominant complex must be included in the program if the program is not to fail by division by zero. The method is simply to choose the equation for which ψ is highest.

In table 3 data for the cupric complexes are presented. $\psi(0)$ has been evaluated for a chloride activity of 10^0 and a copper ion activity of 10^{-6}, and $\psi(-1)$ for the case where the chloride

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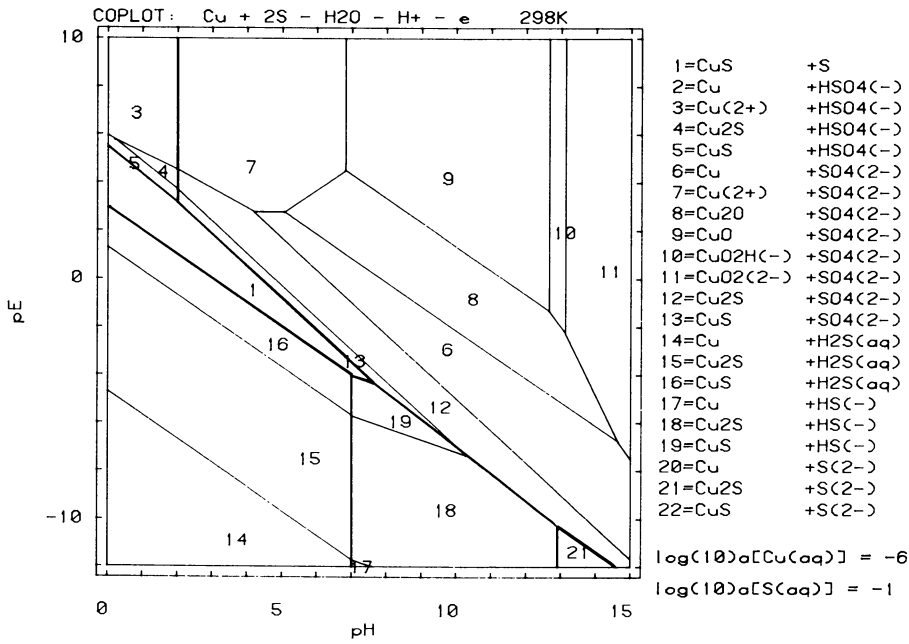

Figure 3. A pH–pE diagram for the Cu–S–H_2O–H^+–e system at 298.15 K where the sulfur is present in excess of copper. The activities of the predominant sulfur and copper solution species are 10^{-1} and 10^{-6}, respectively.

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activity has been changed to 10^{-1}.

Table III

Parameters for chloride complexes of the cupric ion

Equation	$\log_{10}K$	$\psi(0)$	$\psi(-1)$	α	β	α'
$Cu = Cu^{2+} + 2e$	-11.51	-5.51	-5.51	0	2	0
$Cu = CuCl^{+} - Cl^{-} + 2e$	-11.05	-5.05	-6.05	0	2	-1
$Cu = CuCl_2(c) - 2Cl^{-} + 2e$	-15.57	-15.57	-17.57	0	2	-2
$Cu = CuCl_2(aq) - 2Cl^{-} + 2e$	-11.32	-5.32	-7.32	0	2	-2
$Cu = CuCl_3^{-} - 3Cl^{-} + 2e$	-13.72	-7.72	-10.72	0	2	-3
$Cu = CuCl_4^{2-} - 4Cl^{-} + 2e$	-16.05	-10.05	-14.05	0	2	-4

The highest value of $\psi(0)$ (chloride activity 10^{0}) is found for the formation of $CuCl^{+}$, indicating that this compound will dominate all other cupric species under these conditions. However, at a chloride activity of 10^{-1}, only ten times lower, the uncomplexed ion, Cu^{2+}, becomes dominant.

Figure 4 shows a Pourbaix diagram for this case. Even at this relatively low activity the presence of chloride has a profound effect by increasing the stability of cuprous by complex formation, cf figure 2. However, the effect of changing the chloride activity cannot readily be predicted from figure 4 alone. It would be possible to draw families of diagrams on the same plot, each individual diagram corresponding to a particular chloride activity, but diagrams of this kind are very confusing, particularly as in the present case, when the dominant species in certain zones would change from one individual diagram to another. An advantage to the user of a computer-based system of diagram calculation from a databank is that diagrams need be produced only for systems and conditions of direct relevance. There is no need to pack the diagrams with confusing information.

Fortunately a simple solution is available to the problem of representing all the chloride complexes. The algebra of Pourbaix diagrams remains unchanged if $\log a(Cl^{-})$ replaces pH as one of the variables. Figure 5 shows a diagram for the $Cu\text{-}H_2O\text{-}Cl^{-}\text{-}H^{+}\text{-}e$ system under conditions of low pH and low solute activity, where the only stable compounds of copper are copper itself, Cu^{+}, Cu^{2+} or their complexes with Cl^{-}. The new stoichiometry coefficients are listed under α' in table 3. $CuCl_2(c)$ is eliminated because it has a lower value of ψ than $CuCl_2(aq)$ but the same α' and β.

Figure 5 shows that at very high chloride activities the cuprous complex, $CuCl_3^{2-}$, becomes very dominant, being oxidised to cupric complexes only above pE = 10. This information is of value because methods of stabilising particular valence states such as Cu^{+} offer means of separating metals that would be difficult to separate in their normal valence states.

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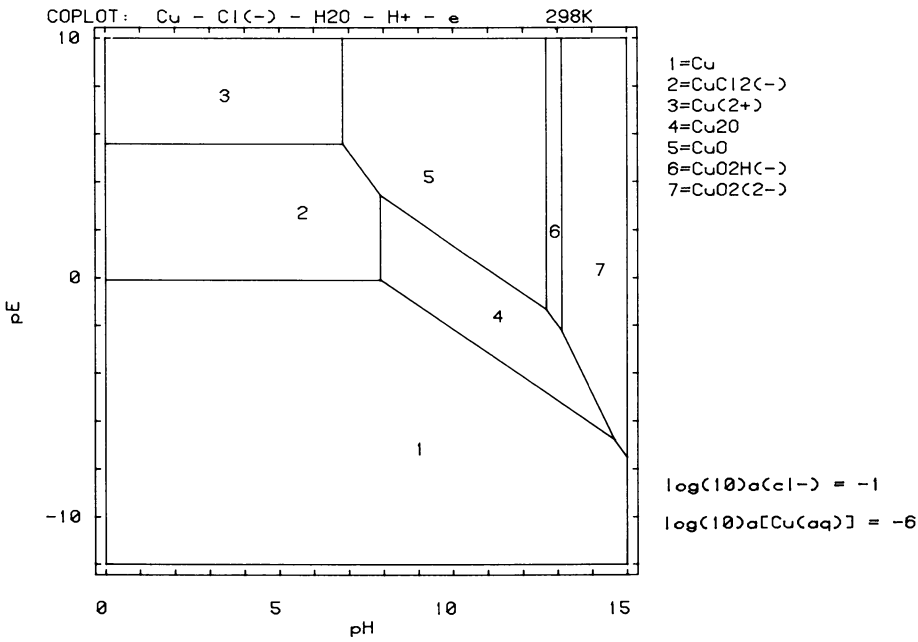

Figure 4. A pH–pE diagram for the Cu–Cl^-–H_2O–H^+–e system at 298.15 K. The activity of Cl^- is 10^{-1}; the activities of the predominant copper solution species are 10^{-6}. The diagram can represent only the most stable chloride complexes of cuprous and cupric and not the proportions of the various complexes.

Table IV

Data used in this paper are taken almost exclusively from the review by Duby(3) in order that diagrams should be consistent with his. ΔG° for CuCl(aq) was estimated from data given by Smith and Martell(6).

Compound	$\Delta_f G^{\circ}$(298K)/kJ mole^{-1}	Compound	$\Delta_f G^{\circ}$(298K)/kJ mole^{-1}
H^+	0	CuO	-127.90
e	0	$HCuO_2^-$	-258.57
H_2O	-237.18	CuO_2^{2-}	-183.68
S	0	Cu_2S	-87.44
HSO_4^-	-756.01	CuS	-53.14
SO_4^{2-}	-744.63	CuCl(c)	-119.66
H_2S	-27.87	CuCl(a)	-96.65
HS^-	12.05	$CuCl_2^-$	-240.16
S^{2-}	85.77	$CuCl_3^{2-}$	-376.56
Cl^-	-131.26	$CuCl^+$	-68.20
Cu	0	$CuCl_2$(c)	-173.64
Cu^+	50.63	$CuCl_2$(a)	-179.90
Cu^{2+}	65.69	$CuCl_3^-$	-315.47
Cu_2O	-147.90	$CuCl_4^{2-}$	-433.46

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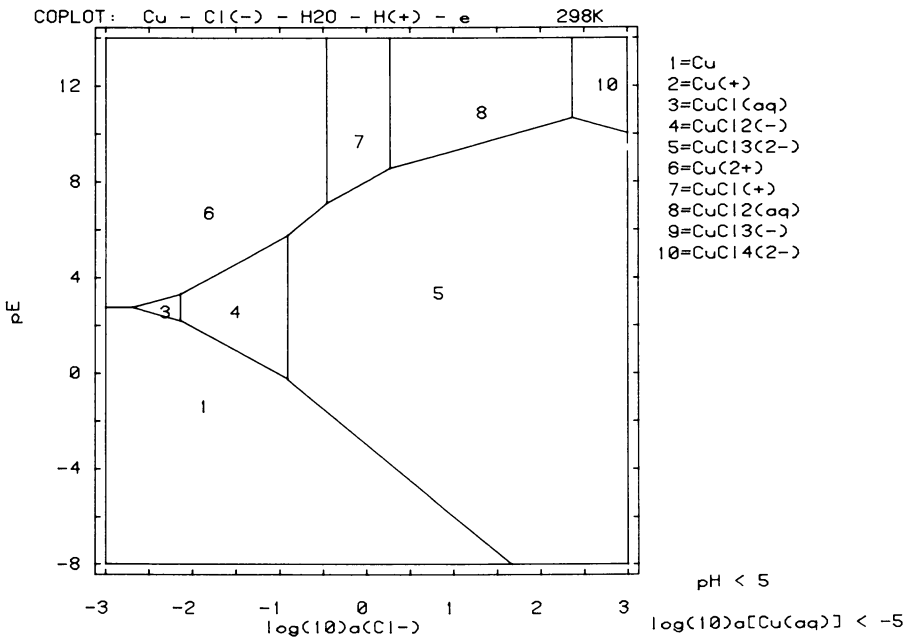

Figure 5. A predominance area diagram for the Cu–Cl^{-1}–H_2O–H^+–e system at 298.15 K analogous to a pH–pE diagram but in which log(10)a(Cl^-) replaces pH as a variable. The pH is less than 5. The activity of the predominant copper solution species are 10^{-6}.

Even this diagram does not give a clear impression of the relative proportions of the various copper compounds present in solution. However, provided no polynuclear species are present, it is a relatively simple matter to use the values of χ to evaluate these proportions and to plot them as a function of a single variable. Figure 6 shows a diagram of this kind using the same data as figure 5 calculated for pE = 10 and variable chloride activity under the assumption that all compounds have the same activity coefficient. It would not be difficult to allow for different values of activity coefficients if these were known.

Program comparisons

The actual program used at NPL was written by N.P. Barry on the basis of the methods described previously. It is written in FORTRAN and has been implemented on IBM 370 and UNIVAC 1100 computers operated by computer bureaux. Vector algebra is employed. The reason why the graphs have double boundaries is that the calculation can be performed for boundaries of any convex polygon of up to 30 sides. This permits calculations to be restricted to the stability range of particular components, for example, that of water or chloride.

Because the program is not coupled to a data base, the input at present comprises values of ψ, α and β for reactions of the reference compound(s). The output comprises the number of lines in the diagram including those of the boundaries, the coordinates of the ends of each line, the number of compounds and the coordinates of the label for each compound in number order. Compounds that are not present are assigned the coordinates 0,0.

The plotting program is written on a Tektronix 4051 graphics micro-computer which is coupled to a 4662 plotter.

A much simpler method of producing Pourbaix diagrams is to divide the coordinate system up into as many points as can conveniently be plotted by a printer. At each point the function χ is then evaluated for each equation 1,i and the value of i determined that gives the highest value of χ. A symbol corresponding to i can then be printed. The method has the virtues that this simple procedure completes the operation and a plotter is not required. This is the basis of the method described by Duby.(3) Its disadvantages are that it is rather slow, it has a poor resolution and the result is not visually satisfying.

A number of other methods have been described as reviewed by Linkson, Phillips and Rowles.(4) Some of these use the point by point method briefly described above and others, using a convex-polygon method, search for the boundaries of one predominance region at a time. An advantage of this approach is that the number of intersections that need to be considered can be reduced substantially as follows. The boundaries of any convex polygon necessarily lie in a sequence of progressively changing slope. Thus testing for intersections with lines in order of their slope

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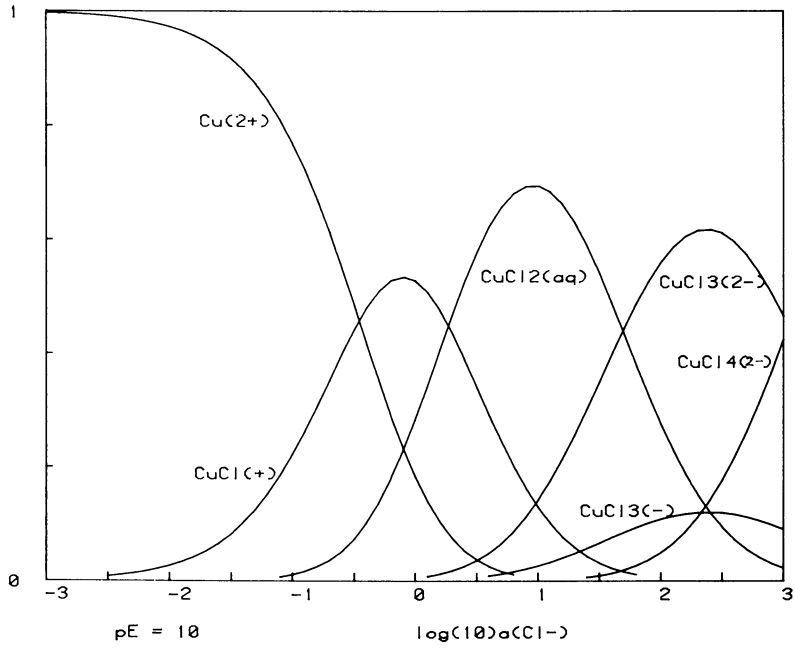

Figure 6. A diagram showing the proportions of various chloride complexes of copper calculated as a function of chloride activity for pH < 5, pE = 10, and copper ion activities less than about 10^{-6}. Note that the cuprous complex $CuCl_3^{2-}$ is dominant at very high chloride activities. The calculation is based on a number of assumptions (see text) that are unlikely to be entirely valid: chloride activities much greater than 100 cannot be achieved readily.

In Thermodynamics of Aqueous Systems with Industrial Applications; Newman, S., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1980.

greatly improves the rate of finding valid intersections. Perhaps the most significant development is that of Turnbull(5) who has linked a computational program to a database. Moreover, up to 5 type 1 compounds can be considered.

In considering the value of different approaches to automatic drawing of Pourbaix diagrams the efficiency of the computer program is only one factor. The simplicity and adequacy of input and output operations are equally or more important. The value of a coupled database is high because it greatly reduces input time and the probability of error. It should not be necessary to call for compounds by formula name for data retrieval since it is clearly possible to call for all the compounds in a given system and to have a means of deleting or adding compounds. This is the method used in the operation of the Gibbs energy minimisation calculations on condensed and gaseous substances using the NPL system MTDATA.

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