Calculation and Analysis of EpH Diagrams Related to the Corrosion of Chinese Bronzes

Arthur D. PELTON
THERMFACT LTD
447 Berwick
Mount-Royal, Québec, H3R 1Z8
Canada

<u>Submitted to</u>: **M. Notis and T. Chase**
Lehigh University

July, 2006

EpH(Pourbaix) diagrams for the Cu-Sn-Cl-H_2O and Cu-Sn-CO_2-H_2O systems are shown in Figs 1-12 and 13-24 respectively for various concentrations of chloride ion (Figs 1-12) or total dissolved CO_2 (Figs 13-24), and for concentrations of other aqueous species of 1.0, 10^{-3} and 10^{-6} molal (mol/kgH_2O). A guide to the figures is given in the List of Figures. The diagrams for the Cu-Sn-CO_2-H_2O system (Figs 13-24) were each prepared by superimposing three diagrams, one for -2<pH<6.27 where the dissolved CO_2 is predominantly in the form of dissolved CO_2 (or H_2CO_3) molecules, one for 6.27<pH<10.23 where HCO_3^- is predominant, and one for 10.23<pH<16 where CO_3^{2-} predominates.

The diagrams were calculated using the FactSage (1) software. Thermodynamic data for all aqueous species were taken from the FactSage FS53 database which is derived principally from NBS data (2). Data for the possible solid products CuO, Cu_2O, SnO, SnO_2, $Cu_3(OH)_2(CO_3)_2$ and $CuCO_3Cu(OH)_2$ were taken from the Helgeson (3) database. Data for all possible solid products containing Cl (CuCl, $CuCl_2$, Cu_4 $(OH)_6Cl_2$, $CuCl_2(H_2O)_2$, $SnCl_2$, $SnOHCl(H_2O)$) were taken from the FactSage FS53 database since they are not found in the more recent Helgeson database. Data for solid Cu, Cu_3Sn and Cu_4Sn were taken from the recent SGTE alloy database (4). When calculations were repeated using data for CuO, Cu_2O, SnO and SnO_2 from the FS53 base rather than the Helgeson base, the results were essentially identical.

Following the usual practice, the diagonal dashed lines on all figures indicate conditions where $P_{O_2} = 1$ bar (upper line) and $P_{H_2} = 1$ bar (lower line). Only the region between these lines is accessible at atmospheric pressure.

Corrosion products containing tin

It can be seen that solid SnO_2 is the stable Sn-containing phase everywhere between the $P_{O_2} = 1$ and $P_{H_2} = 1$ lines in all figures except in a couple of cases at very low pH and under very reducing conditions Tin is present in metallic form in the compound Cu_3Sn(s) only below the $P_{H_2} = 1$ line.

Metastable Cu_4Sn

Calculations were repeated replacing Cu_3Sn by the metastable intermetallic phase Cu_4Sn. The calculated diagrams are virtually identical to those with Cu_3Sn. A sample calculation is shown in Fig. 4c which may be compared to Fig. 4. That is, the difference in thermodynamic stability of Cu_3Sn and Cu_4Sn is very slight.

Diagram with no intermetallics

A "base" diagram was also calculated with Cu and Sn as the only metallic phases. That is, all intermetallics Cu_aSn_b were suppressed. The diagram is shown in Fig. 4d and may be compared to Figs. 4 and 4c.

Copper activity less than 1.0

The copper phase in the Jin bronzes contains some dissolved Sn, so the activity of metallic Cu is less than unity. Depending on the Sn content, the copper activity could vary from 1.0 to about 0.8. When the calculations were repeated for a copper activity of 0.8, the resultant diagrams were virtually unchanged. (Since the diagrams have logarithmic scales, changing the Cu activity by a factor of 0.8 has very little effect).

Copper-containing solid phases

The solid copper-containing phases which are calculated to have stable phase fields are CuO, Cu_2O, $CuCl$, $Cu_4(OH)_6Cl_2$ (that is, $3Cu(OH)_2CuCl_2$ paratacamite) and $CH_2O_5Cu_2$ (that is, $CuCO_3Cu(OH)_2$, malachite), in good agreement with the observed corrosion products of the bronzes (5) except for the absence of $Ca_3(OH)_2(CO_3)_2$ (azurite). As stated above, the Helgeson database (3) was used for malachite and azurite. In the older NBS database (2), the thermodynamic properties of azurite are nearly identical to those in the Helgeson database, but azurite has a somewhat lower Gibbs energy in the NBS base. When the calculations were repeated with the NBS data, azurite appeared with a stable field but malachite was absent. A sample calculation is shown in Fig. 22a which can be compared with Fig. 22. Under all conditions (Figs 13-24), the extent of the azurite field calculated with NBS data is nearly the same as the extent of the malachite field calculated with Helgeson data, and these fields are of about the same extent as the combined (azurite + malachite) field calculated by Pourbaix (6). That is, these two solids have very similar stabilities and, within the error limits of the data, one or the other, or both, could be stable.

$CuCl_3^-$ ions not included

The NBS database contains data for the $CuCl_3^-$ aqueous ion. However, this was not included in the present calculations. If included in the calculations, this ion has a stable phase field at low pH and high oxidation potential. A sample calculation is shown in Fig. 4a which may be compared to Fig. 4 where the $CuCl_3^-$ ion was not included in the calculations. The effect of including the ion is to displace the phase boundary of first appearance of $Cu_4(OH)_6Cl_2$ to higher pH. (Essentially, the Cu^{2+} ions are complexed by Cl^- to form the $CuCl_3^-$ complex ion, thereby stabilizing copper in the aqueous phase.) I have not seen this ion mentioned elsewhere and, indeed, Pourbaix (5) did not consider it in his calculation of the Cu-Cl-H_2O diagrams. Consequently, in the calculations in Figs 1-12 this ion has not been included in the calculations. However, one should note that such complexing of Cu^{2+} by Cl^- might occur, thereby displacing the formation of $Cu_4(OH)_6Cl_2$ to higher pH values. This effect would, of course, be greater at higher Cl^- concentrations.

$Cu(OH)_2$ solid and $CuCO_3$ solid not included

The NBS database contains data for solid $Cu(OH)_2$. This solid was not included in the present calculations. If included, its effect is to replace the CuO (tenorite) field and extend this field somewhat to lower pH values, as illustrated in Figs. 4b and 22b which should be compared to

Figs 4 and 22a respectively. Essentially, $Cu(OH)_2$ is hydrated CuO (that is, $CuOH_2O$), with the hydration energy rendering it slightly more stable. This product is not mentioned by Wang (5) as being observed in the corrosion of the Jin bronzes.

The NBS base also contains data for solid $CuCO_3$ which, if included, has a small calculated stable phase field under certain conditions. However, this unhydrated carbonate is not observed (5) in the corrosion of the Jin bronzes, and so was not included in the present calculations.

Effect of temperature

The temperature dependences of the thermodynamic data are not well known. Hence, calculations at temperatures other than 298.15 K are unreliable. Sample calculations performed at 313.15 K are shown in Figs 4e and 22c which should be compared to Figs 4 and 22 respectively. Since there are no data whatsoever for the heat capacity of $Cu_4(OH)_6Cl_2$, its phase field on Fig. 4e was simply estimated.

The Cu-Sn-Cl-CO_2-H_2O system

The FactSage software cannot yet calculate diagrams when Cl^- and dissolved CO_2 are present simultaneously. Hence, in the present report, diagrams are presented for the Cu-Sn-Cl-H_2O and Cu-Sn-CO_2-H_2O systems separately.

When both chloride and CO_2 are present, the following procedure should be used to identify the stable corrosion products. Select the two diagrams from Figs 1-12 and 13-24 which correspond to the desired m(Cl^-) and m(total dissolved CO_2) (both, of course, for the same molality of other aqueous species, m(aqueous species).) Select a point on the diagrams given by a value of the E and pH coordinates. If, at this point, the same corrosion products are shown as being stable on both diagrams, then, of course, these are the stable products. If, at the point in question, CuCl(s) appears on the chloride diagram, then this is the stable phase. If the point in question falls within a field where $Cu_4(OH)_6Cl_2$ is stable on the chloride series of diagrams and where $CH_2O_5(Cu)_2$ is not stable on the carbonate series, then $Cu_4(OH)_6Cl_2$ is stable. Conversely, if the point falls on a field where $CH_2O_5(Cu)_2$ is stable and $Cu_4(OH_6)Cl_2$ is not stable, then $CH_2O_5(Cu)_2$ is stable.

The only problem arises when the (E, pH) coordinate point in question falls within the stable $Cu_4(OH)_6Cl_2$ field on the chloride series of diagrams and within the stable $CH_2O_5(Cu)_2$ field on the carbonate series. According to the Phase Rule, both solid phases cannot simultaneously appear. To determine which is the more stable, the following rule-of-thumb can be used. Compare the chloride molality, m(Cl^-), to the total dissolved CO_2 molality, m(total dissolved CO_2). If m(Cl^-) is greater than m(total CO_2) then $Cu_4(OH_6)Cl_2$ is probably more stable than $CH_2O_5(Cu)_2$. If m(total CO_2) is greater than m(Cl^-) then $CH_2O_5(Cu)_2$ is probably more stable than $Cu_4(OH_6)Cl_2$. If the difference is two orders of magnitute or more, then this rule-of-thumb is almost certainly valid. For differences of one order of magnitute or less, the validity of the rule is less certain.

References

1. www.factsage.com

2. NBS Series 270, (1968-71)
3. GEOPIG-SUPCRC (Helgeson) Public Database (version 2003)
4. www.sgte.org
5. Q. Wang, "Metalworking Technology and Deterioration of Jin Bronzes from the Tianna-Qucun Site, Shanxi, China", BAR International Series 1023, (2002).
6. M. Pourbaix, "Electrochemical Corrosion and Reduction", NBS Special Publication 479, (1977)

List of Figures

System Cu-Sn-Cl-H_2O

System Cu-Sn-CO_2-H_2O

Figure No.	m (CO_2) mol/kgH_2O	m(aqueous species) mol/kgH_2O	Comments
13	10^{-3} (44 ppm)	1.0	
14	"	10^{-3}	
15	"	10^{-6}	
16	10^{-2} (440 ppm)	1.0	
17	"	10^{-3}	
18	"	10^{-6}	
19	10^{-1} (4400 ppm)	1.0	
20	"	10^{-3}	
21	"	10^{-6}	
22	1.0 (44000 ppm)	1.0	
22a	"	1.0	NBS data
22b	"	1.0	NBS data including $Cu(OH)_2(s)$
22c	"	1.0	T = 313.15 K
23	"	10^{-3}	
24	"	10^{-6}	

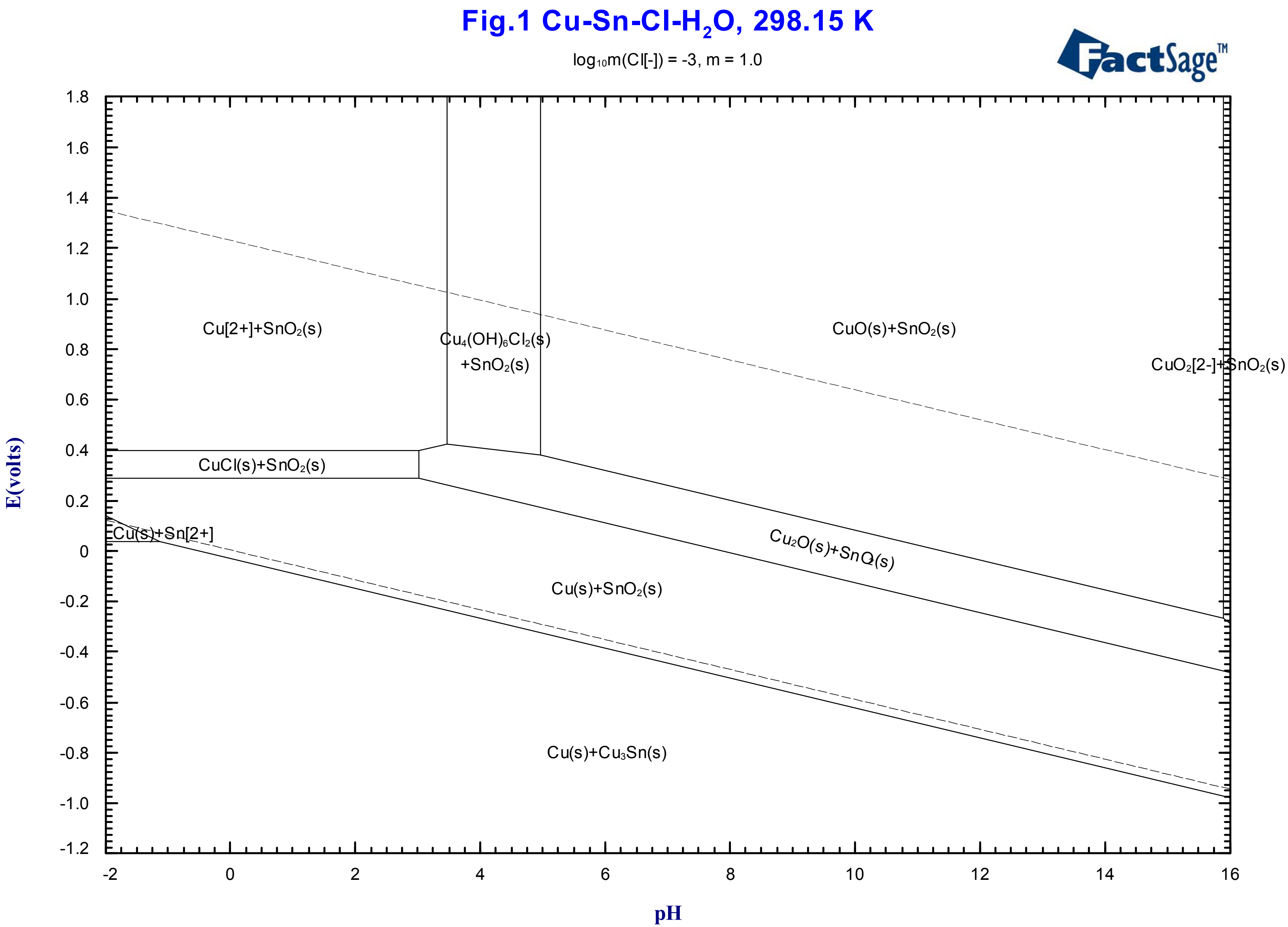


Fig.1 Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = -3, m = 1.0
FactSage™
Cu[2+]+SnO2(s)
Cu4(OH)6Cl2(s)
+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
CuCl(s)+SnO2(s)
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

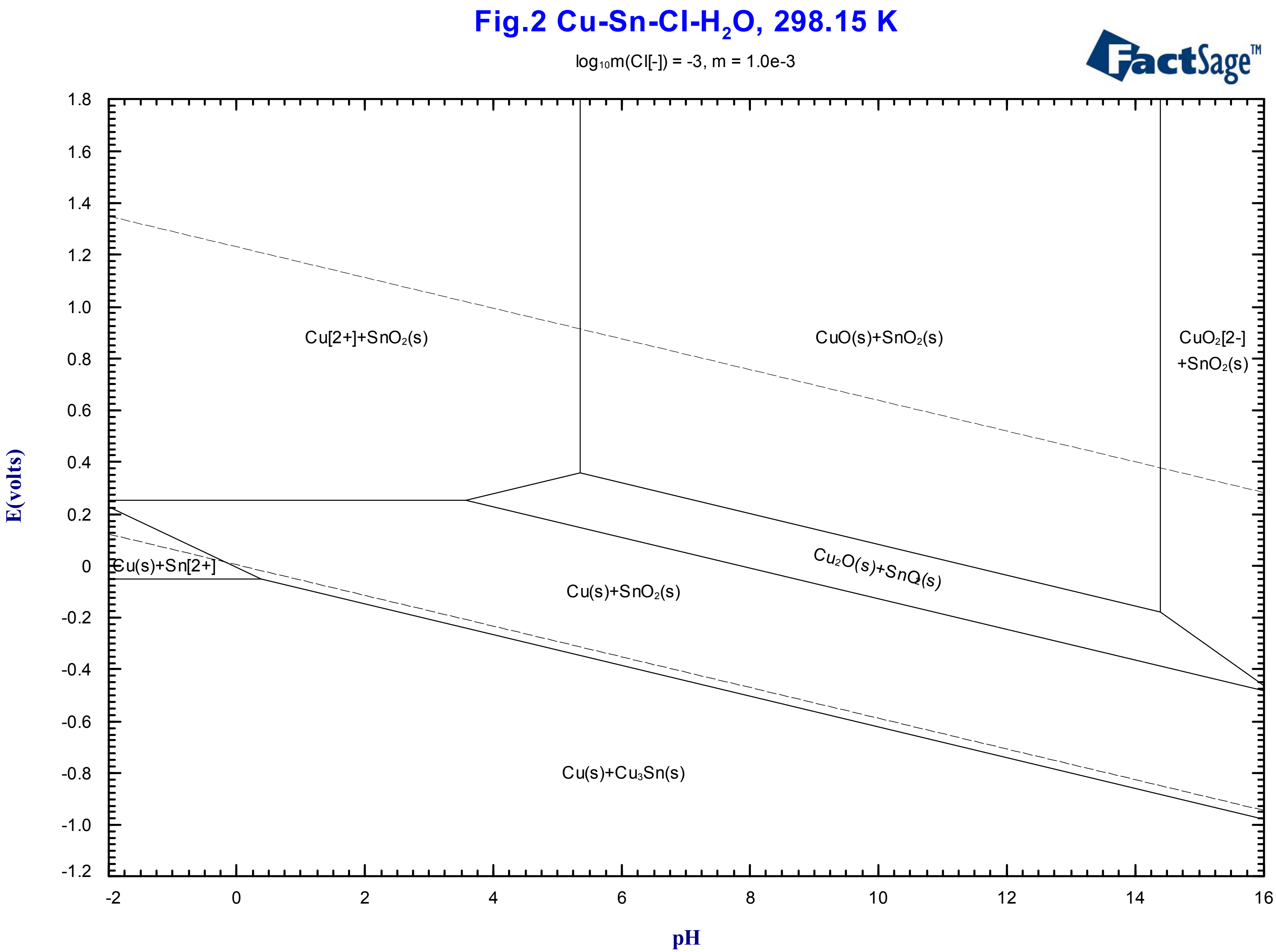


Fig.2 Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = -3, m = 1.0e-3
FactSage™
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
E(volts)
Cu[2+]+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]
+SnO2(s)
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
-2
0
2
4
6
8
10
12
14
16
pH

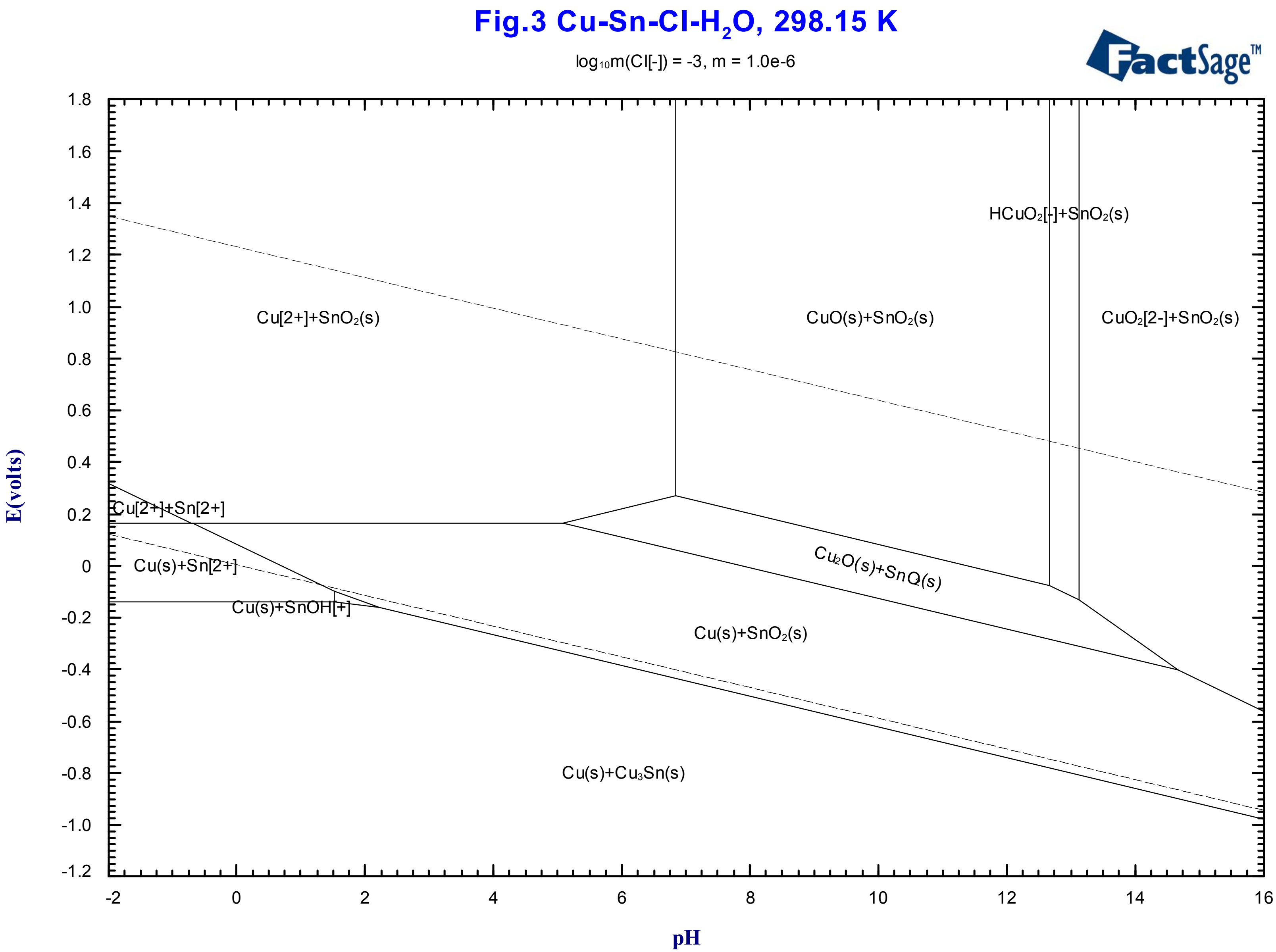


Fig.3 Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = -3, m = 1.0e-6
FactSage™
HCuO2[-]+SnO2(s)
Cu[2+]+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
Cu[2+]+Sn[2+]
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnOH[+]
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

Fig.4 Cu-Sn-Cl-H_2O, 298.15 K

$\log_{10}m(Cl[-]) = -2$, m = 1.0

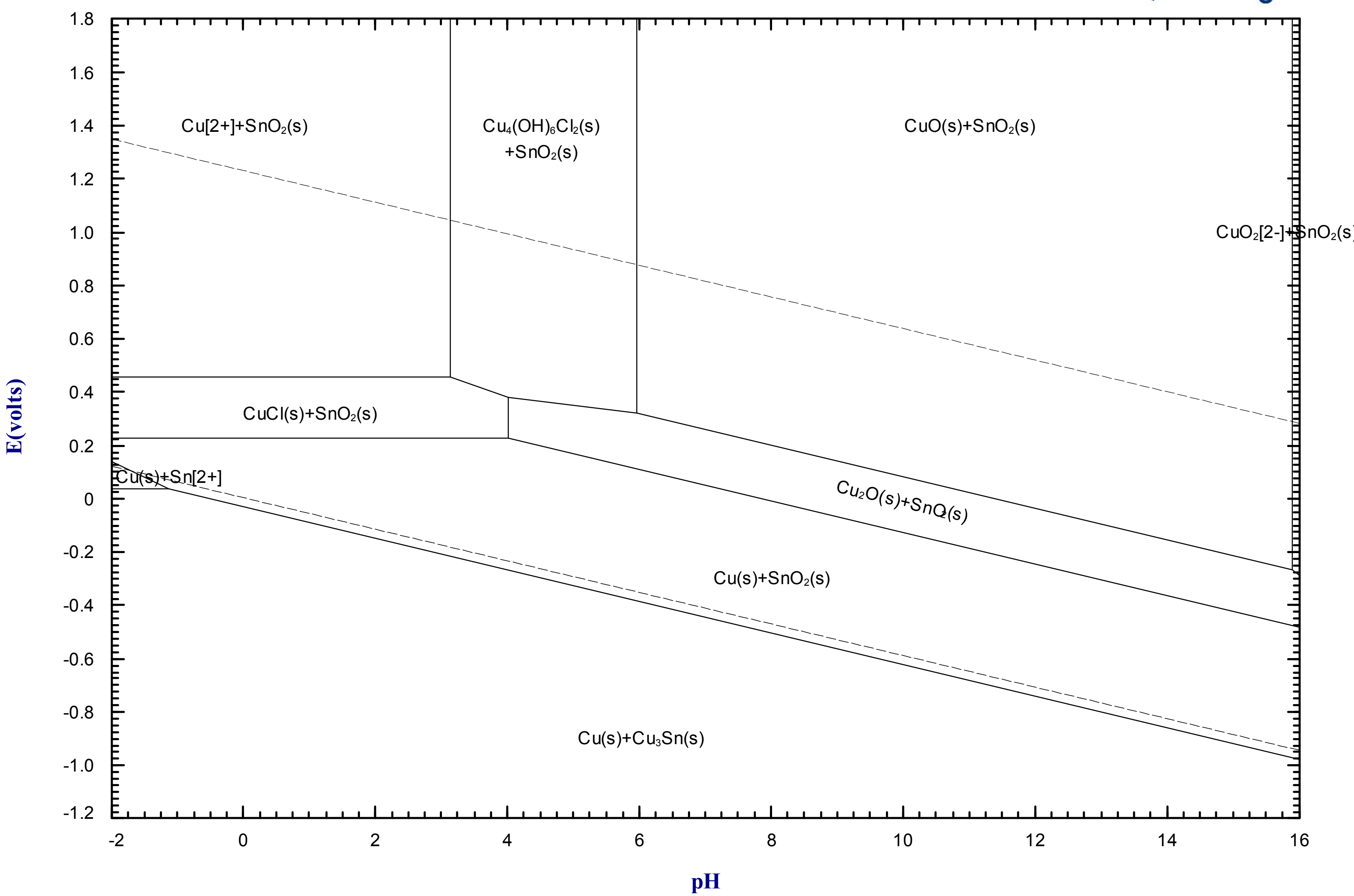
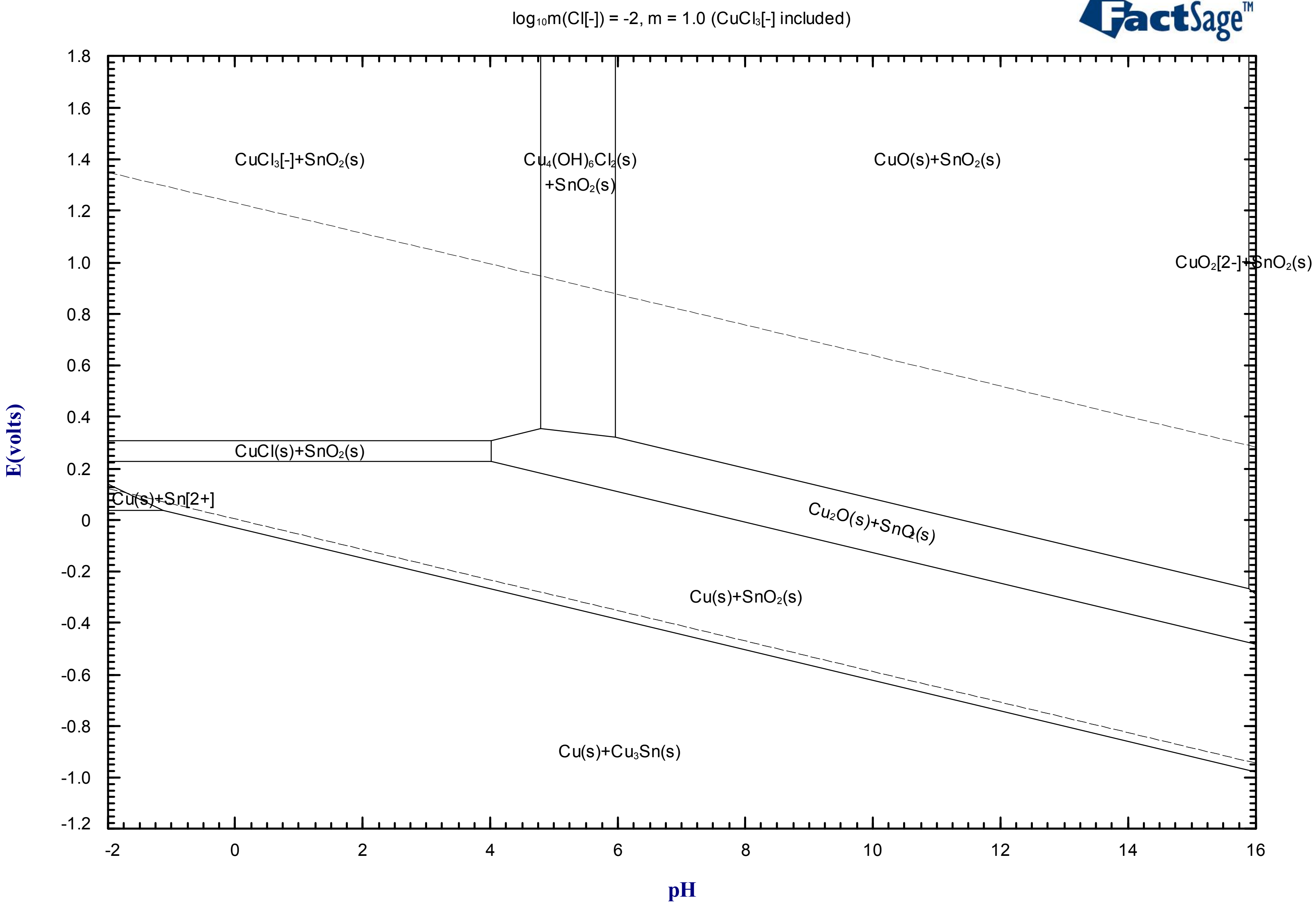


Fig.4a Cu-Sn-Cl-H_2O, 298.15 K



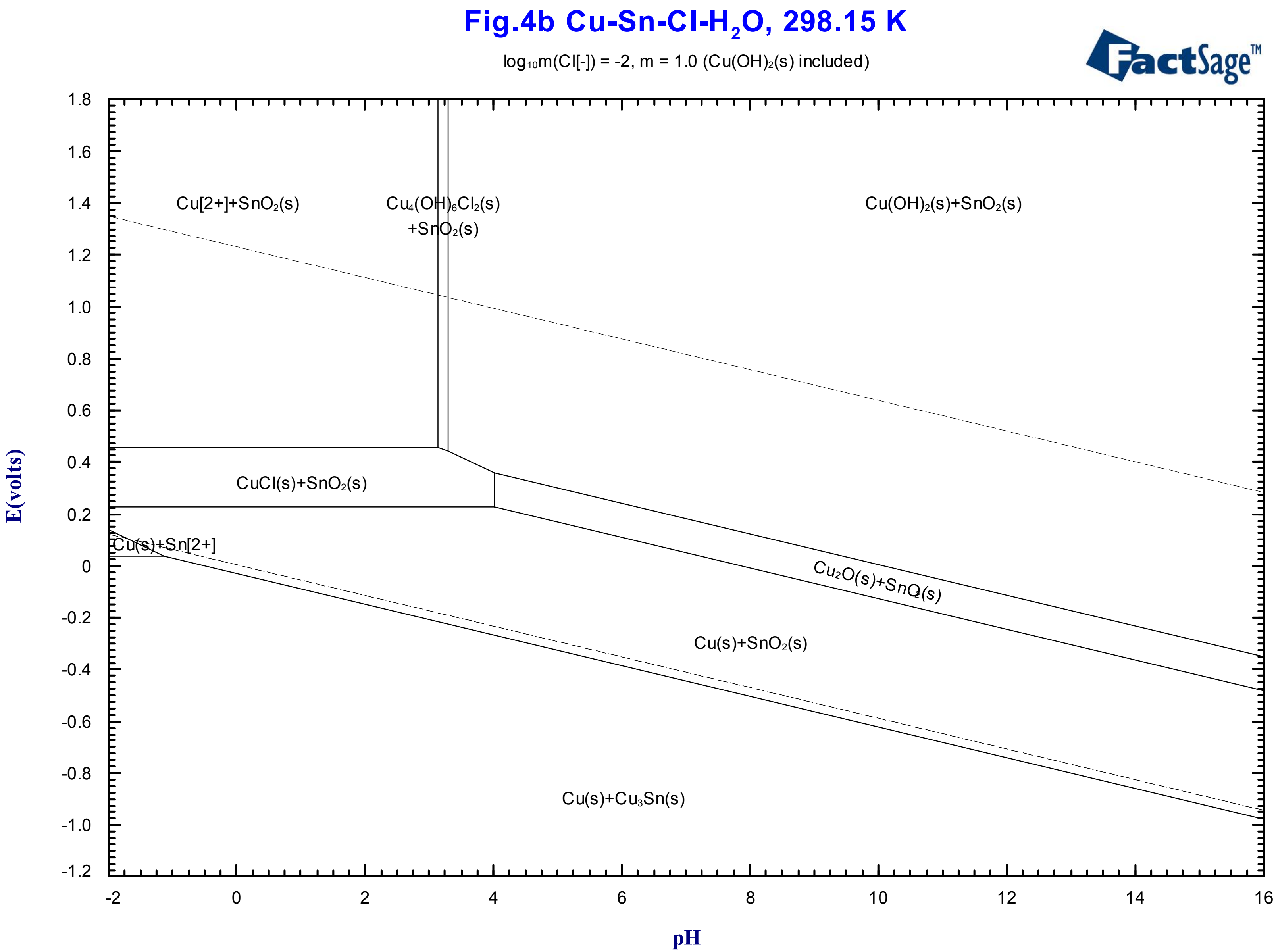


Fig.4b Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = -2, m = 1.0 (Cu(OH)2(s) included)
Cu[2+]+SnO2(s)
Cu4(OH)6Cl2(s)
+SnO2(s)
Cu(OH)2(s)+SnO2(s)
CuCl(s)+SnO2(s)
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

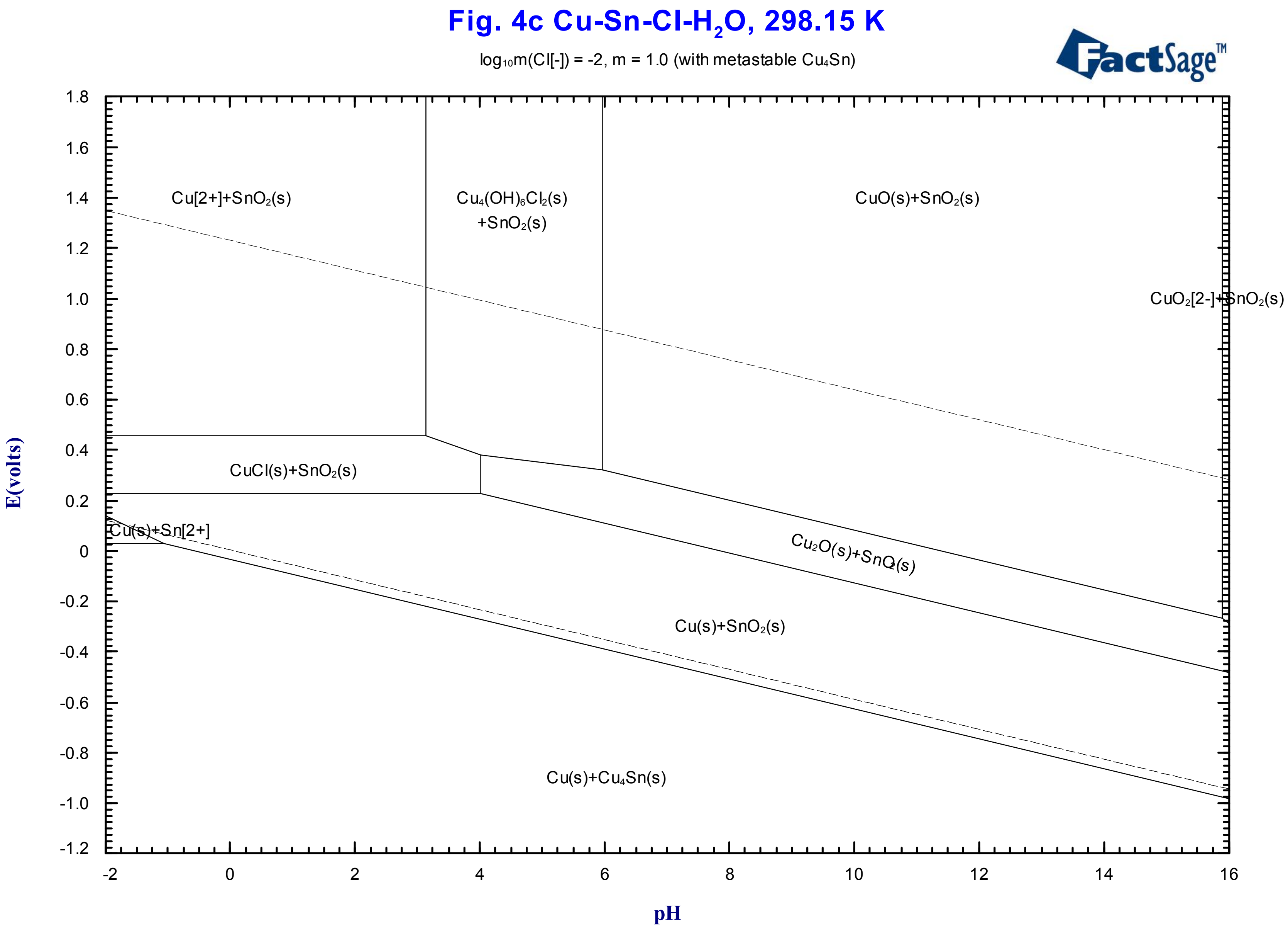


Fig. 4c Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = -2, m = 1.0 (with metastable Cu4Sn)
FactSage™
Cu[2+]+SnO2(s)
Cu4(OH)6Cl2(s)
+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
CuCl(s)+SnO2(s)
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu4Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

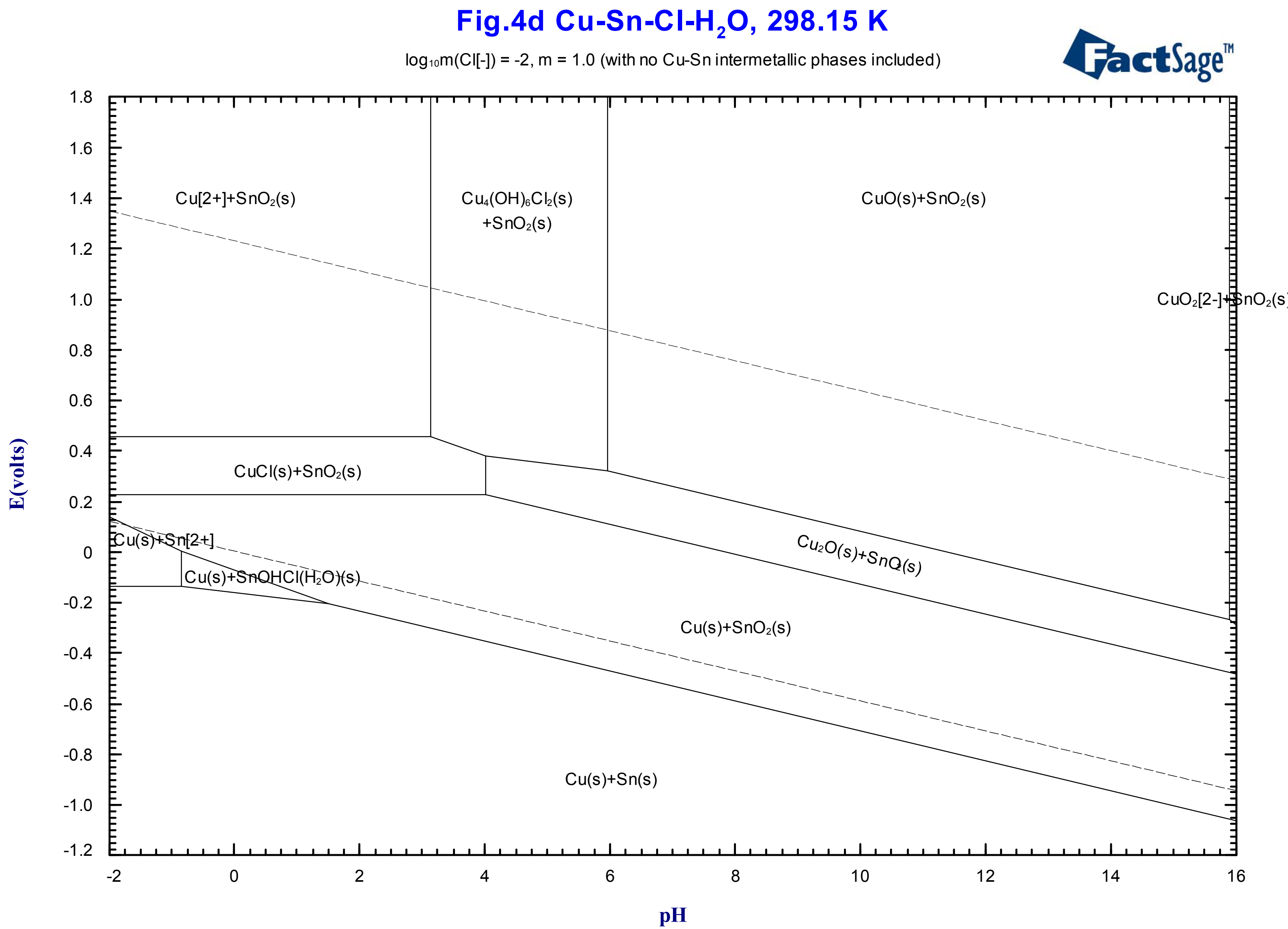


Fig.4d Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = -2, m = 1.0 (with no Cu-Sn intermetallic phases included)
FactSage™
Cu[2+]+SnO2(s)
Cu4(OH)6Cl2(s)
+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
CuCl(s)+SnO2(s)
Cu(s)+Sn[2+]
Cu(s)+SnOHCl(H2O)(s)
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

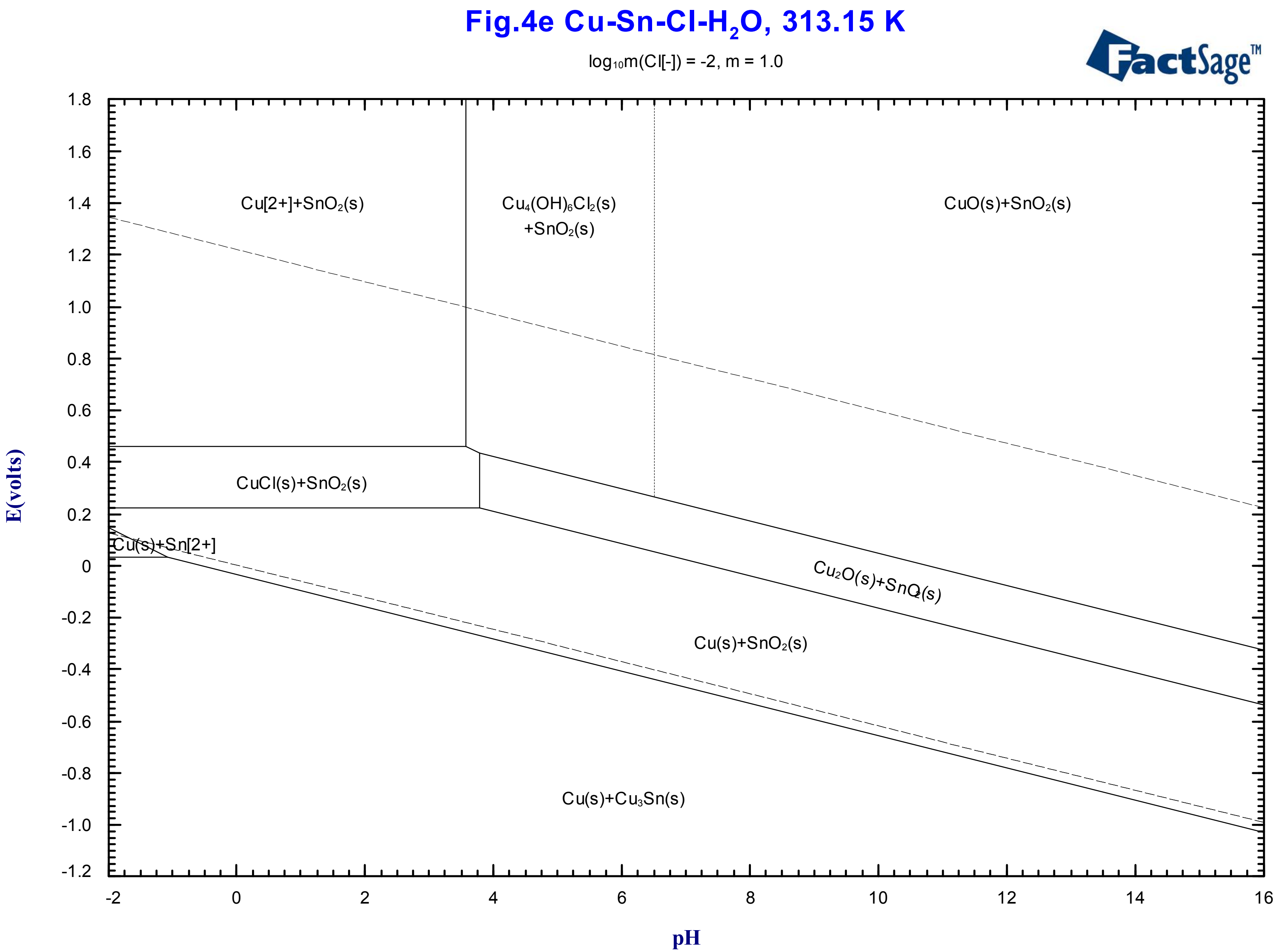


Fig.4e Cu-Sn-Cl-H2O, 313.15 K
log10m(Cl[-]) = -2, m = 1.0
FactSage™
Cu[2+]+SnO2(s)
Cu4(OH)6Cl2(s)
+SnO2(s)
CuO(s)+SnO2(s)
CuCl(s)+SnO2(s)
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

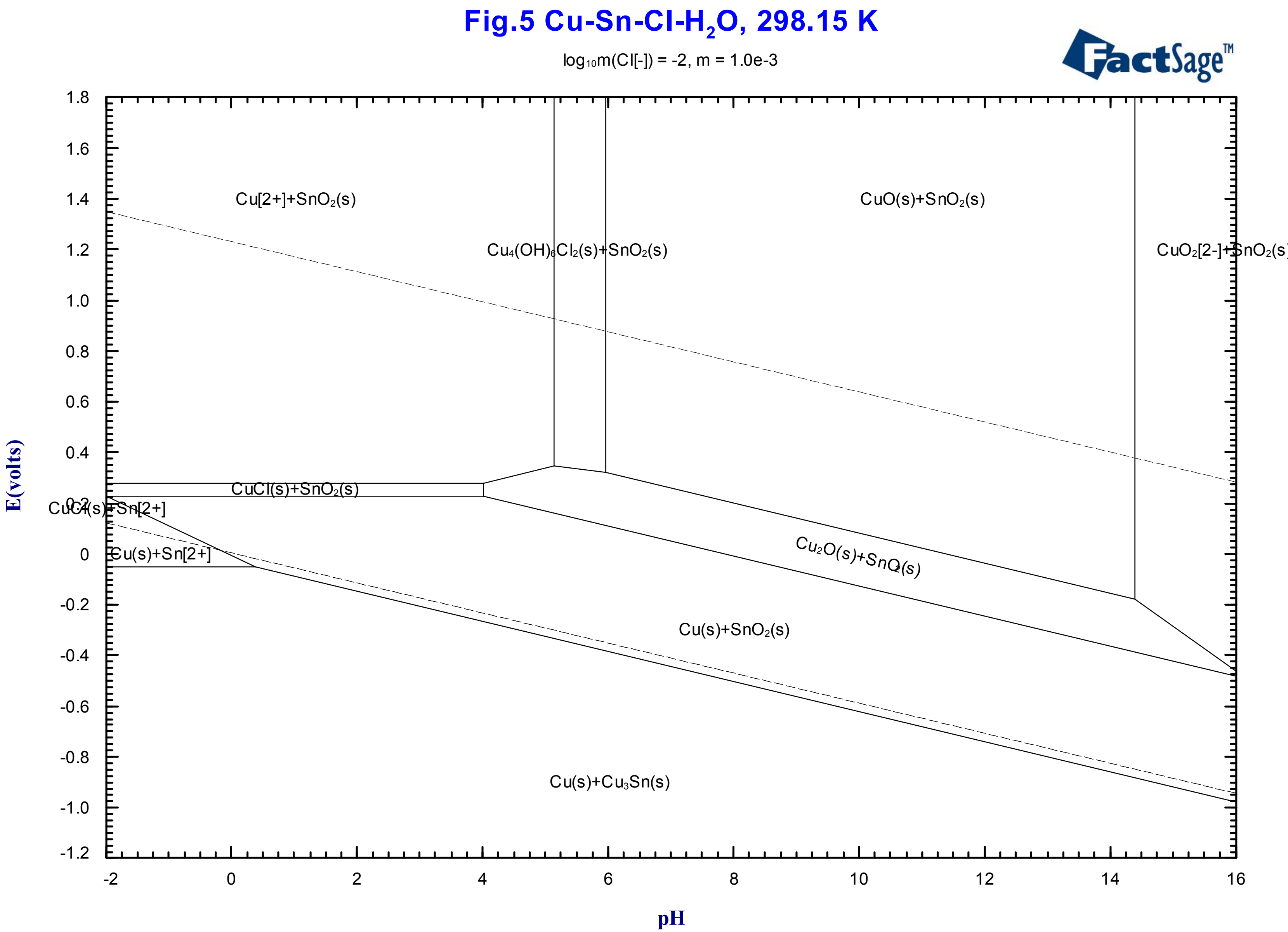


Fig.5 Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = -2, m = 1.0e-3
Cu[2+]+SnO2(s)
CuO(s)+SnO2(s)
Cu4(OH)6Cl2(s)+SnO2(s)
CuO2[2-]+SnO2(s)
CuCl(s)+SnO2(s)
CuCl(s)+Sn[2+]
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

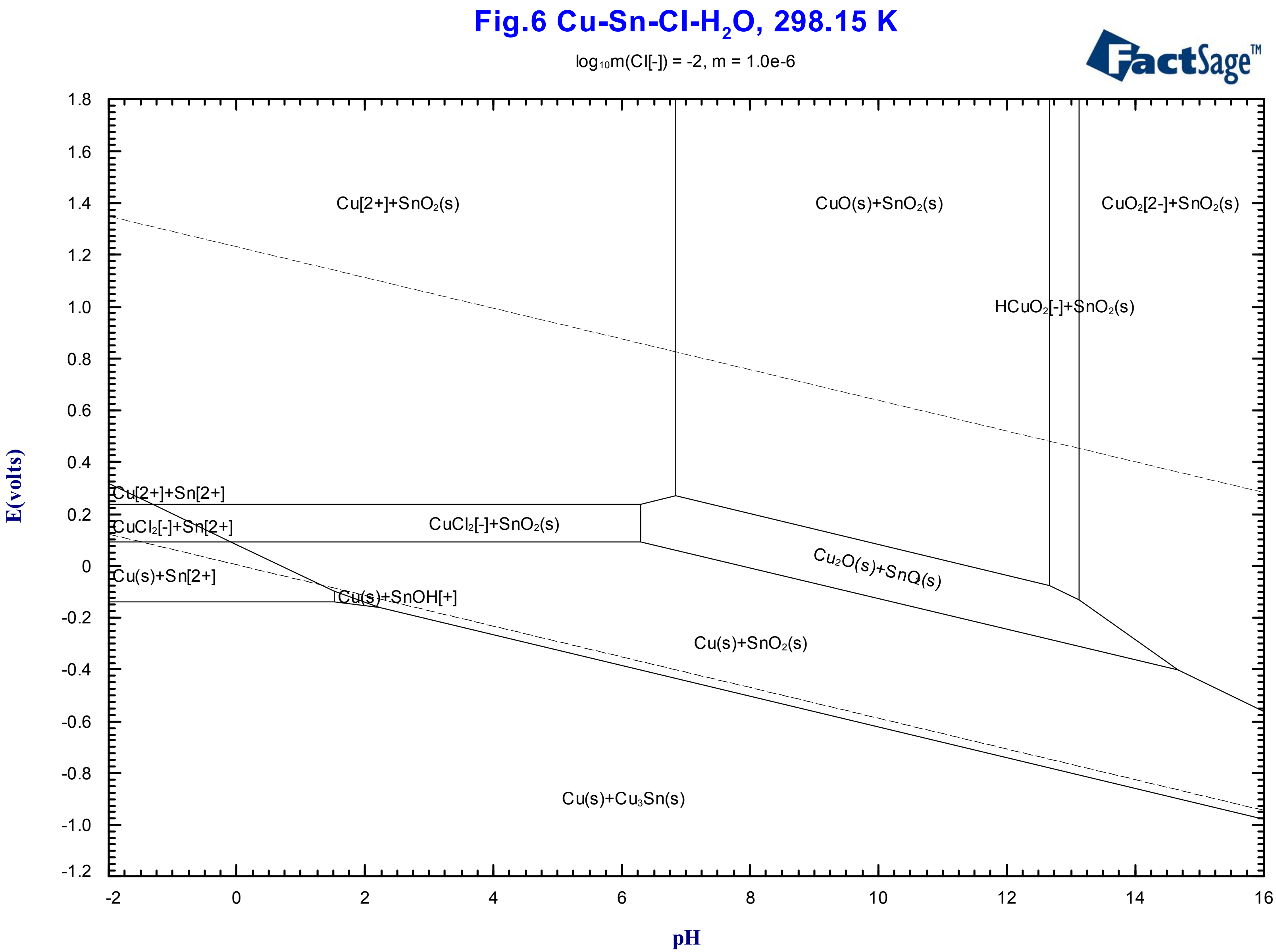


Fig.6 Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = -2, m = 1.0e-6
Cu[2+]+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
HCuO2[-]+SnO2(s)
Cu[2+]+Sn[2+]
CuCl2[-]+Sn[2+]
CuCl2[-]+SnO2(s)
Cu(s)+Sn[2+]
Cu(s)+SnOH[+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH

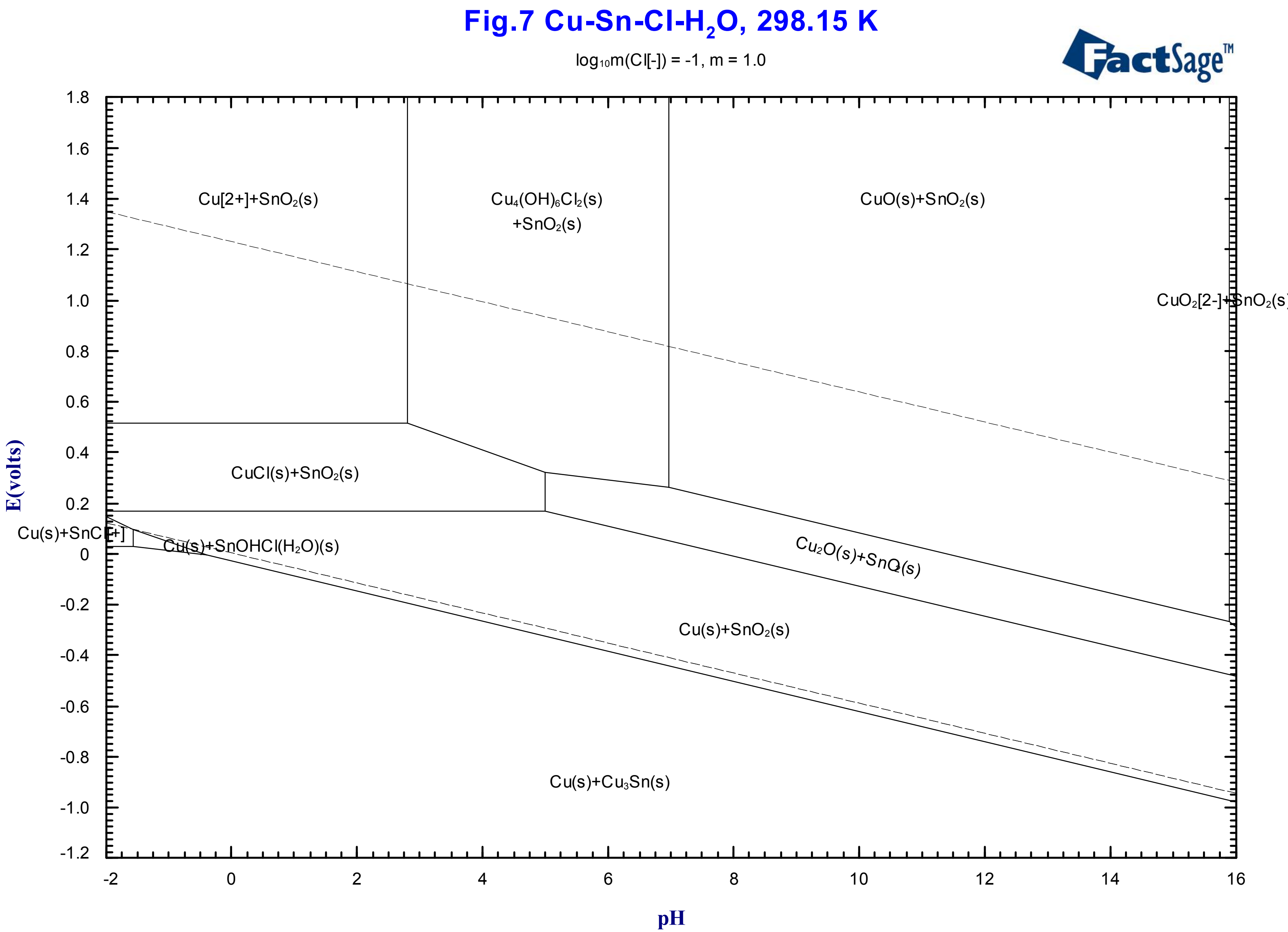


Fig.7 Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = -1, m = 1.0
FactSage™
Cu[2+]+SnO2(s)
Cu4(OH)6Cl2(s)
+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
CuCl(s)+SnO2(s)
Cu(s)+SnCl[+]
Cu(s)+SnOHCl(H2O)(s)
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

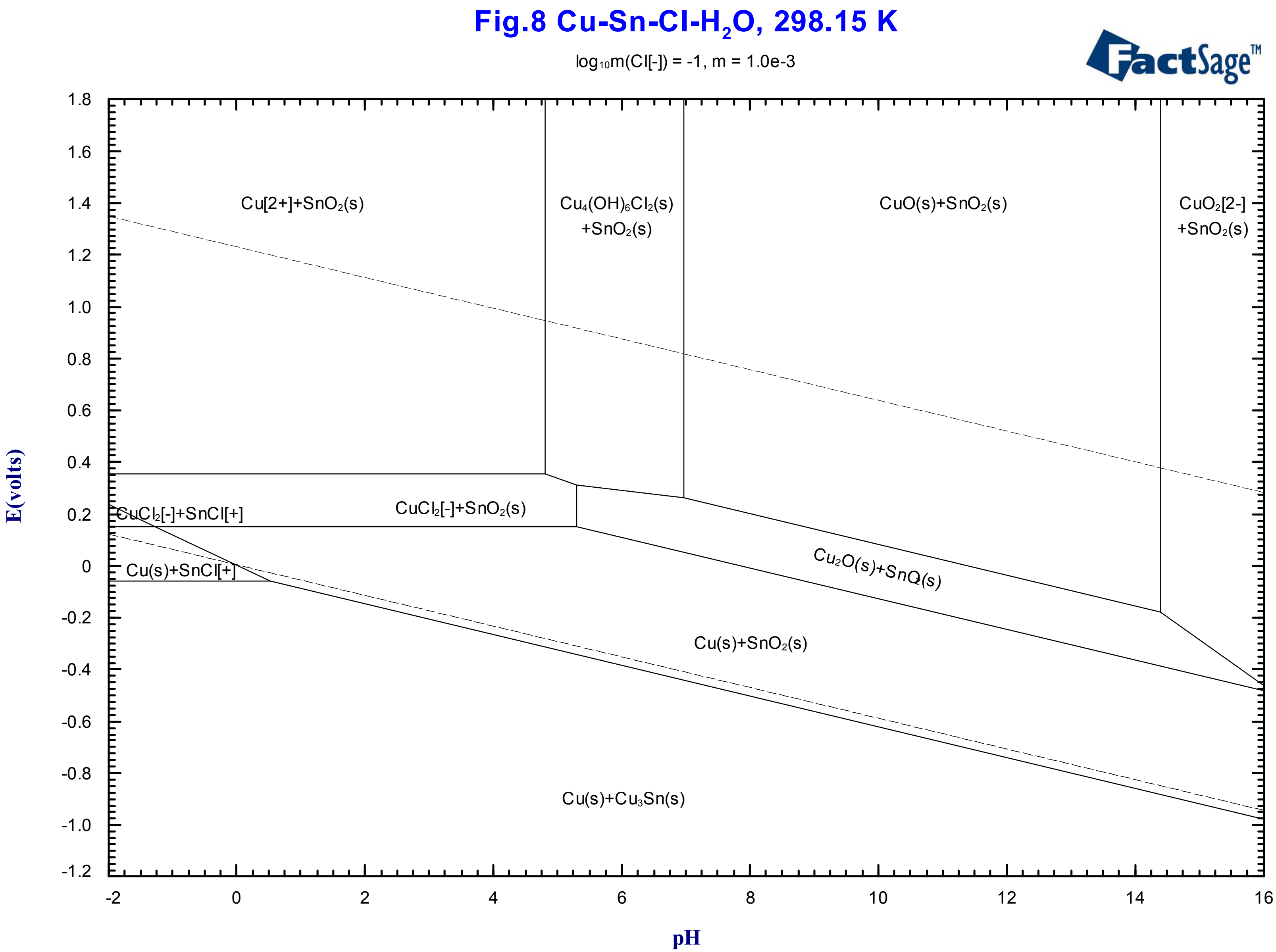


Fig.8 Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = -1, m = 1.0e-3
FactSage™
Cu[2+]+SnO2(s)
Cu4(OH)6Cl2(s)
+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]
+SnO2(s)
CuCl2[-]+SnCl[+]
CuCl2[-]+SnO2(s)
Cu(s)+SnCl[+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

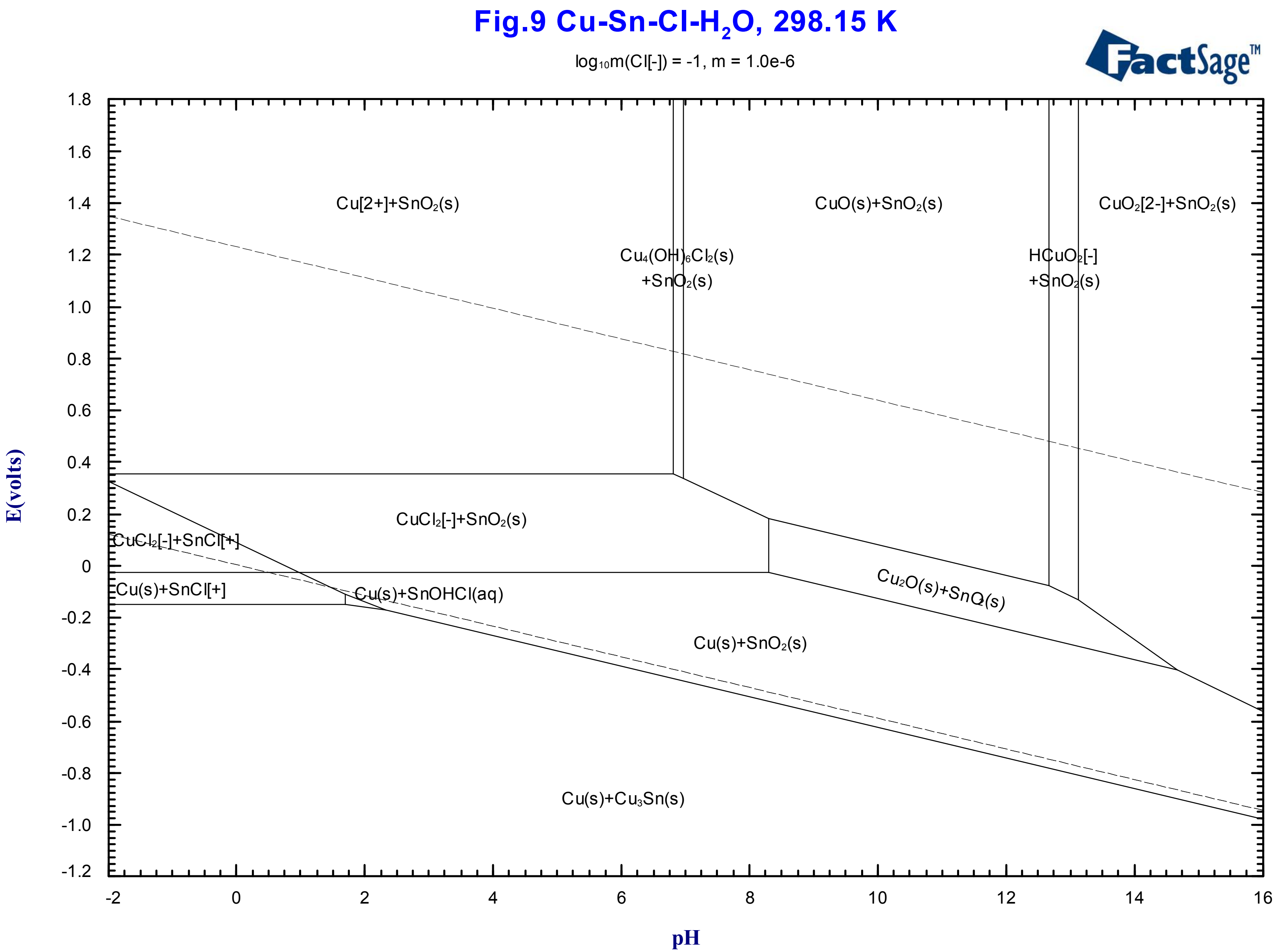


Fig.9 Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = -1, m = 1.0e-6
Cu[2+]+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
Cu4(OH)6Cl2(s)
+SnO2(s)
HCuO2[-]
+SnO2(s)
CuCl2[-]+SnO2(s)
CuCl2[-]+SnCl[+]
Cu(s)+SnCl[+]
Cu(s)+SnOHCl(aq)
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH

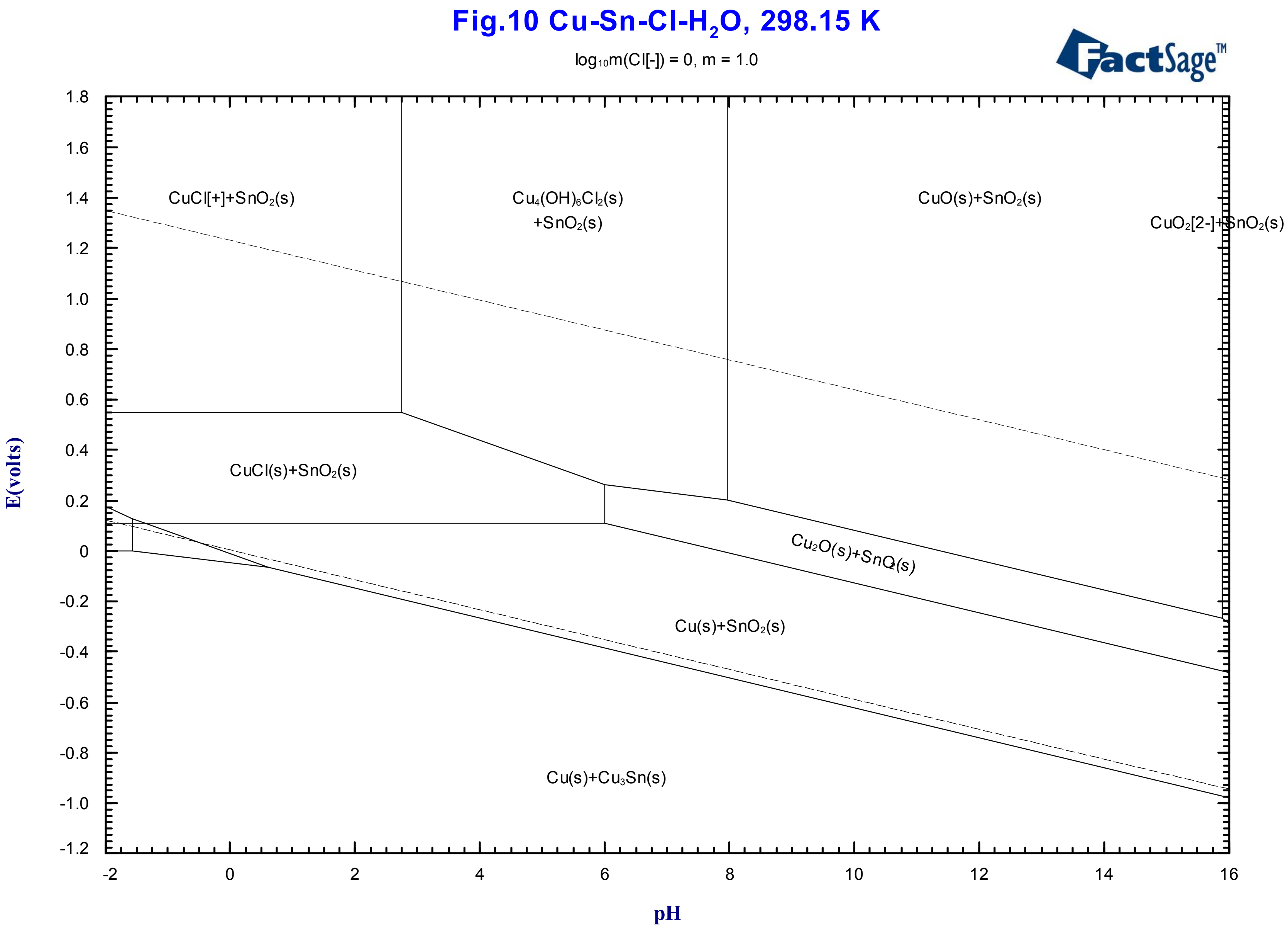


Fig.10 Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = 0, m = 1.0
CuCl[+]+SnO2(s)
Cu4(OH)6Cl2(s)
+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
CuCl(s)+SnO2(s)
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

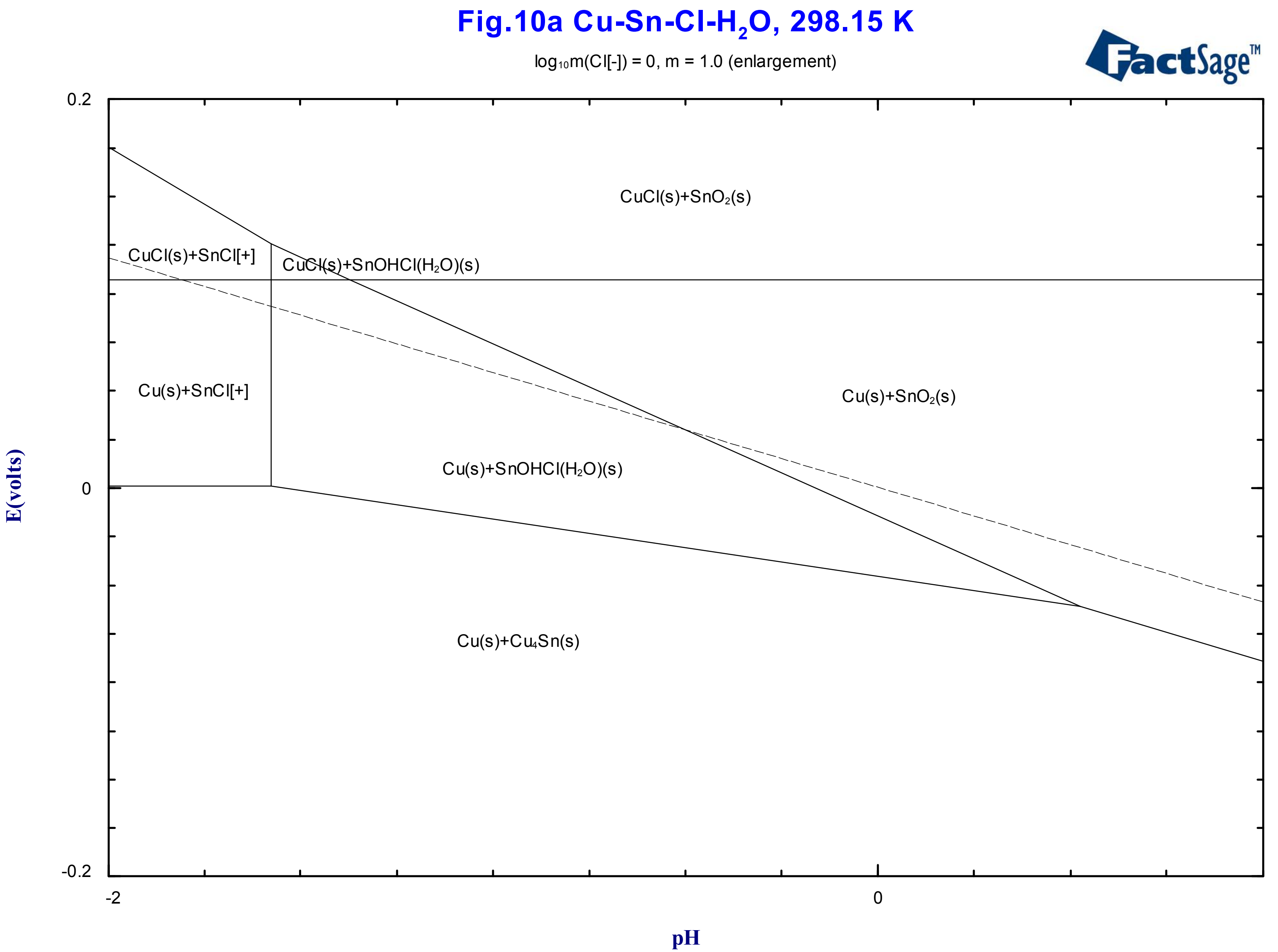


Fig.10a Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = 0, m = 1.0 (enlargement)
FactSage™
0.2
0
-0.2
-2
0
E(volts)
pH
CuCl(s)+SnO2(s)
CuCl(s)+SnCl[+]
CuCl(s)+SnOHCl(H2O)(s)
Cu(s)+SnCl[+]
Cu(s)+SnO2(s)
Cu(s)+SnOHCl(H2O)(s)
Cu(s)+Cu4Sn(s)

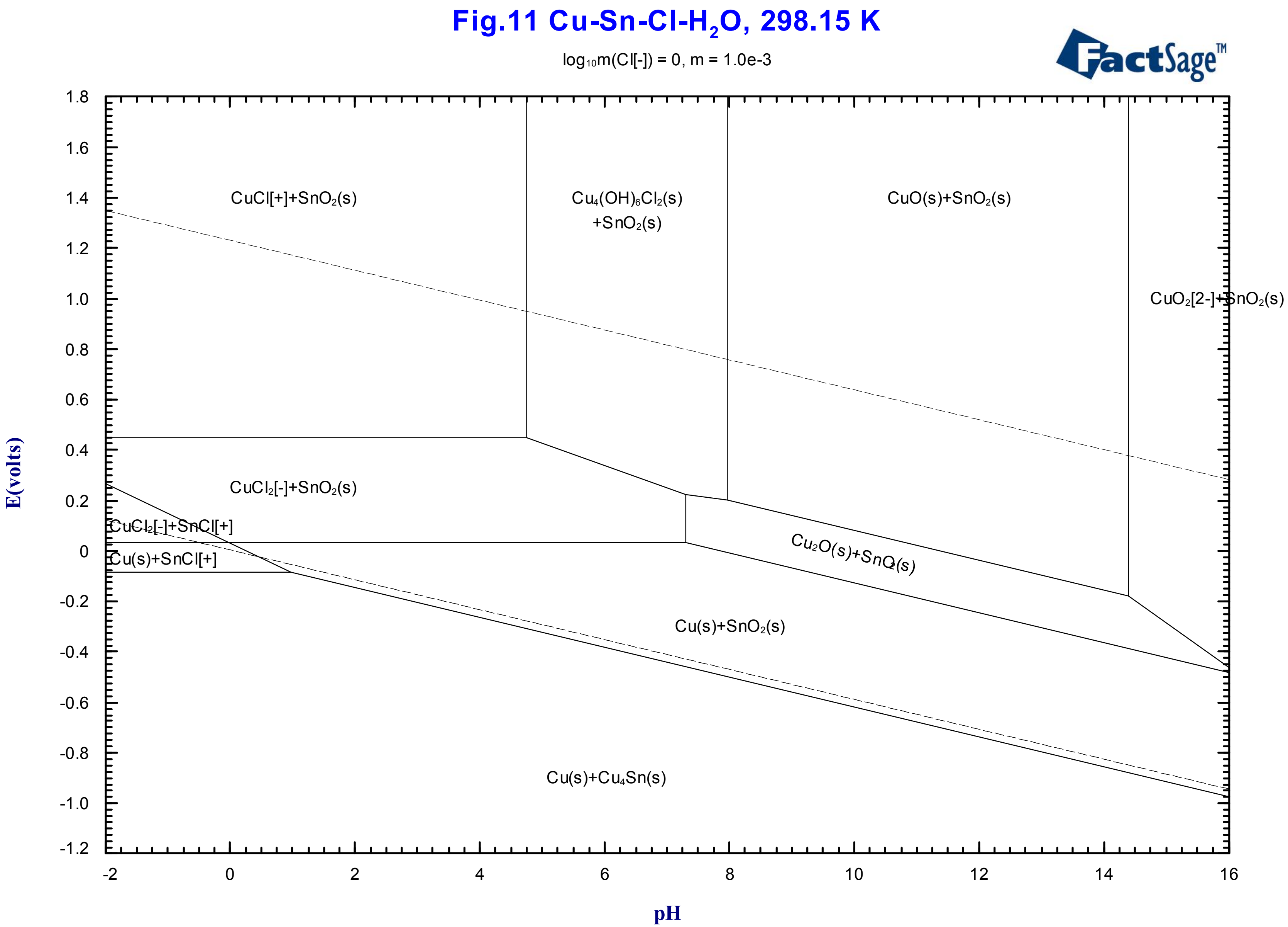


Fig.11 Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = 0, m = 1.0e-3
FactSage™
CuCl[+]+SnO2(s)
Cu4(OH)6Cl2(s)
+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
CuCl2[-]+SnO2(s)
CuCl2[-]+SnCl[+]
Cu(s)+SnCl[+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu4Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

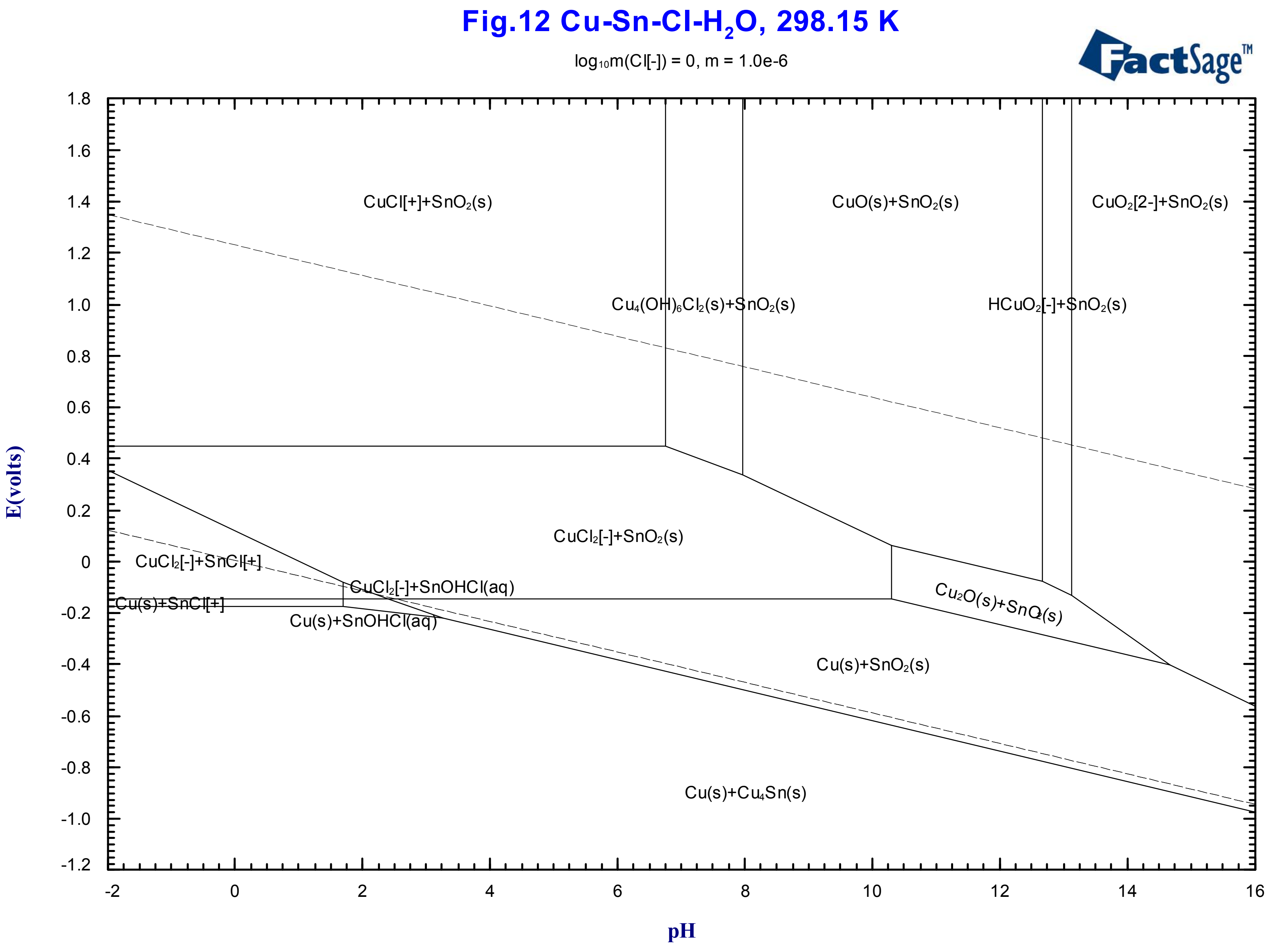


Fig.12 Cu-Sn-Cl-H2O, 298.15 K
log10m(Cl[-]) = 0, m = 1.0e-6
CuCl[+]+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
Cu4(OH)6Cl2(s)+SnO2(s)
HCuO2[-]+SnO2(s)
CuCl2[-]+SnO2(s)
CuCl2[-]+SnCl[+]
CuCl2[-]+SnOHCl(aq)
Cu(s)+SnCl[+]
Cu(s)+SnOHCl(aq)
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu4Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

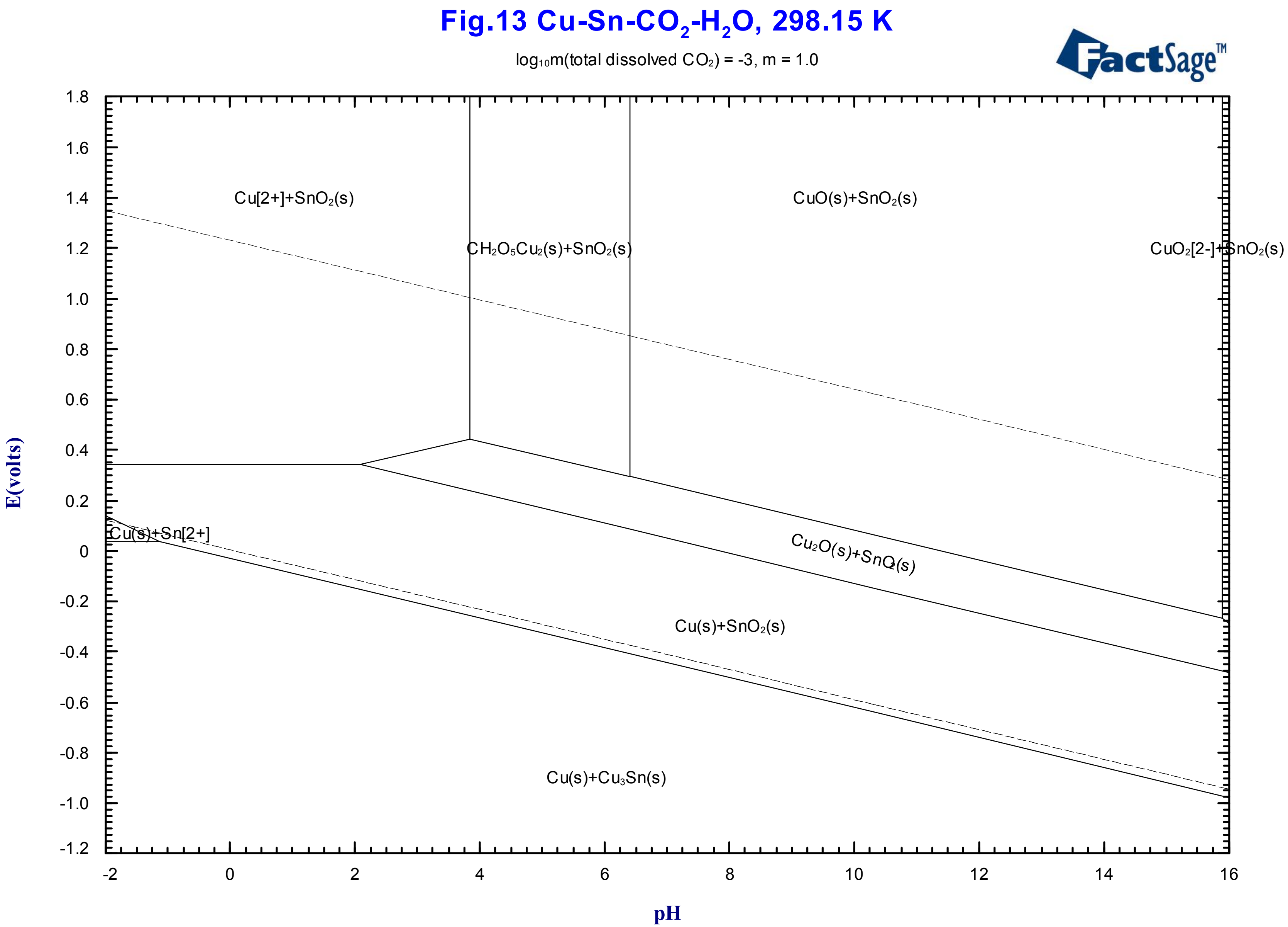


Fig.13 Cu-Sn-CO2-H2O, 298.15 K
log10m(total dissolved CO2) = -3, m = 1.0
E(volts)
pH
Cu[2+]+SnO2(s)
CuO(s)+SnO2(s)
CH2O5Cu2(s)+SnO2(s)
CuO2[2-]+SnO2(s)
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

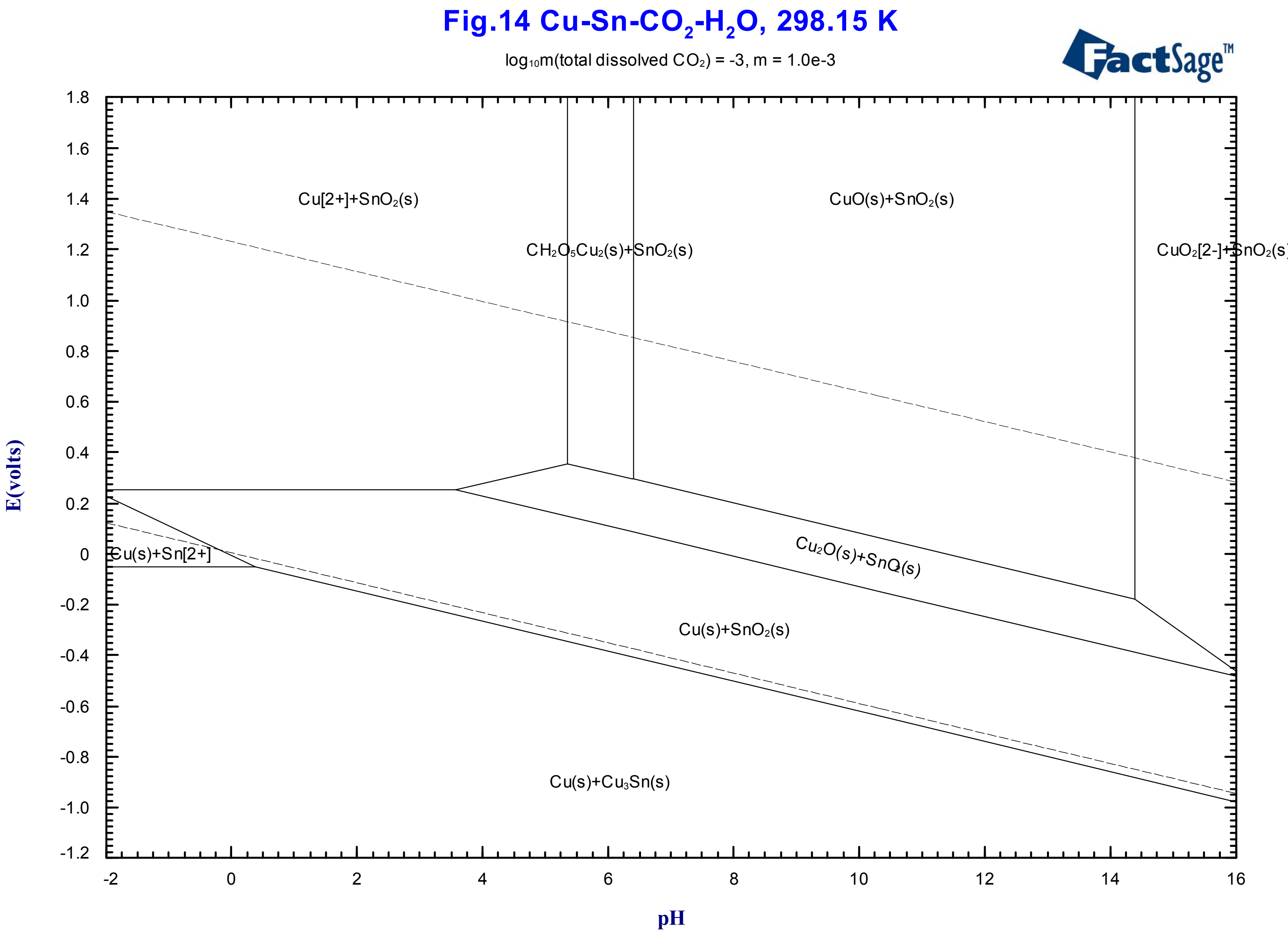


Fig.14 Cu-Sn-CO2-H2O, 298.15 K
log10m(total dissolved CO2) = -3, m = 1.0e-3
Cu[2+]+SnO2(s)
CuO(s)+SnO2(s)
CH2O5Cu2(s)+SnO2(s)
CuO2[2-]+SnO2(s)
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

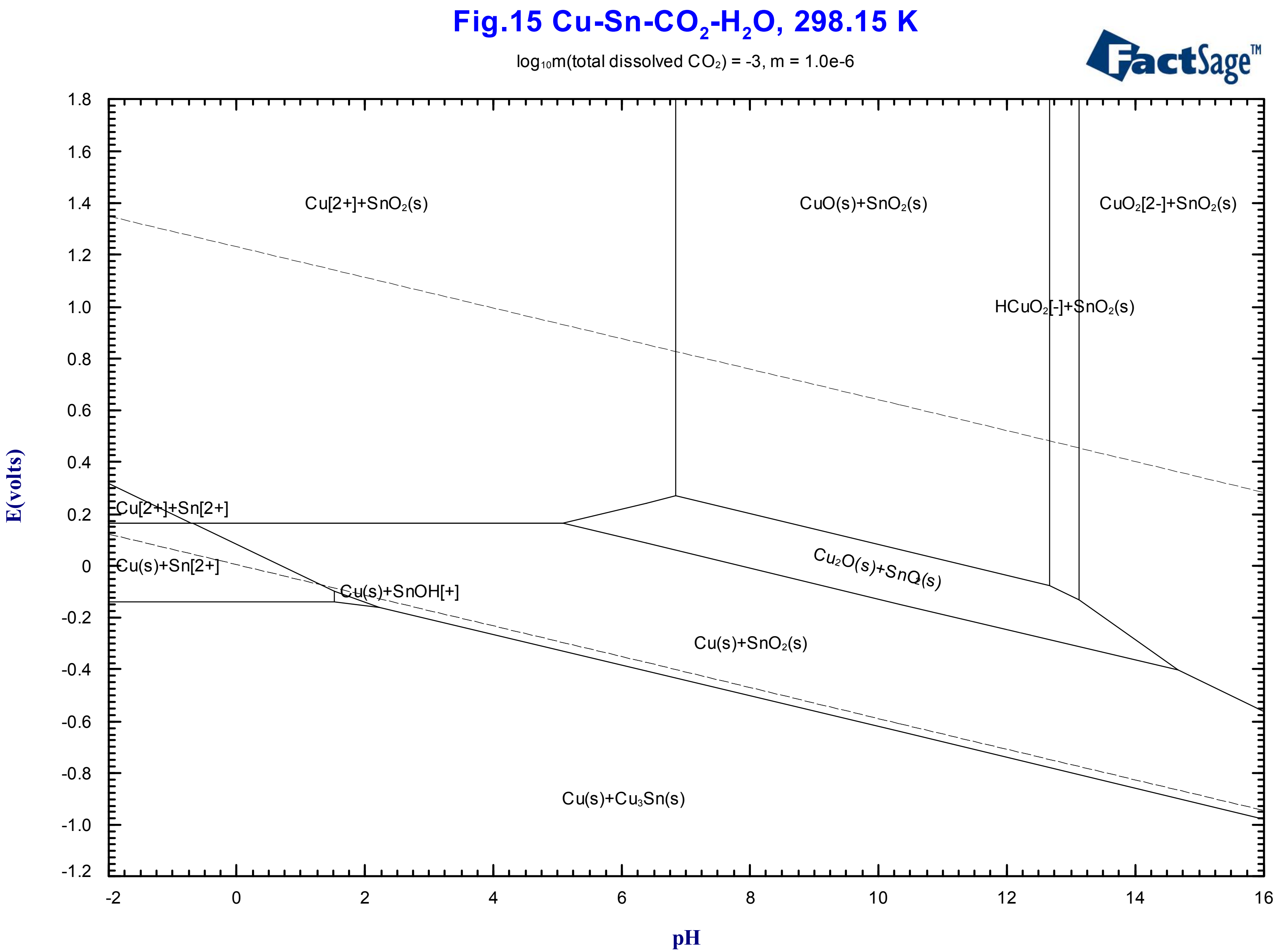


Fig.15 Cu-Sn-CO2-H2O, 298.15 K
log10m(total dissolved CO2) = -3, m = 1.0e-6
FactSage™
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16
Cu[2+]+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
HCuO2[-]+SnO2(s)
Cu[2+]+Sn[2+]
Cu(s)+Sn[2+]
Cu(s)+SnOH[+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)

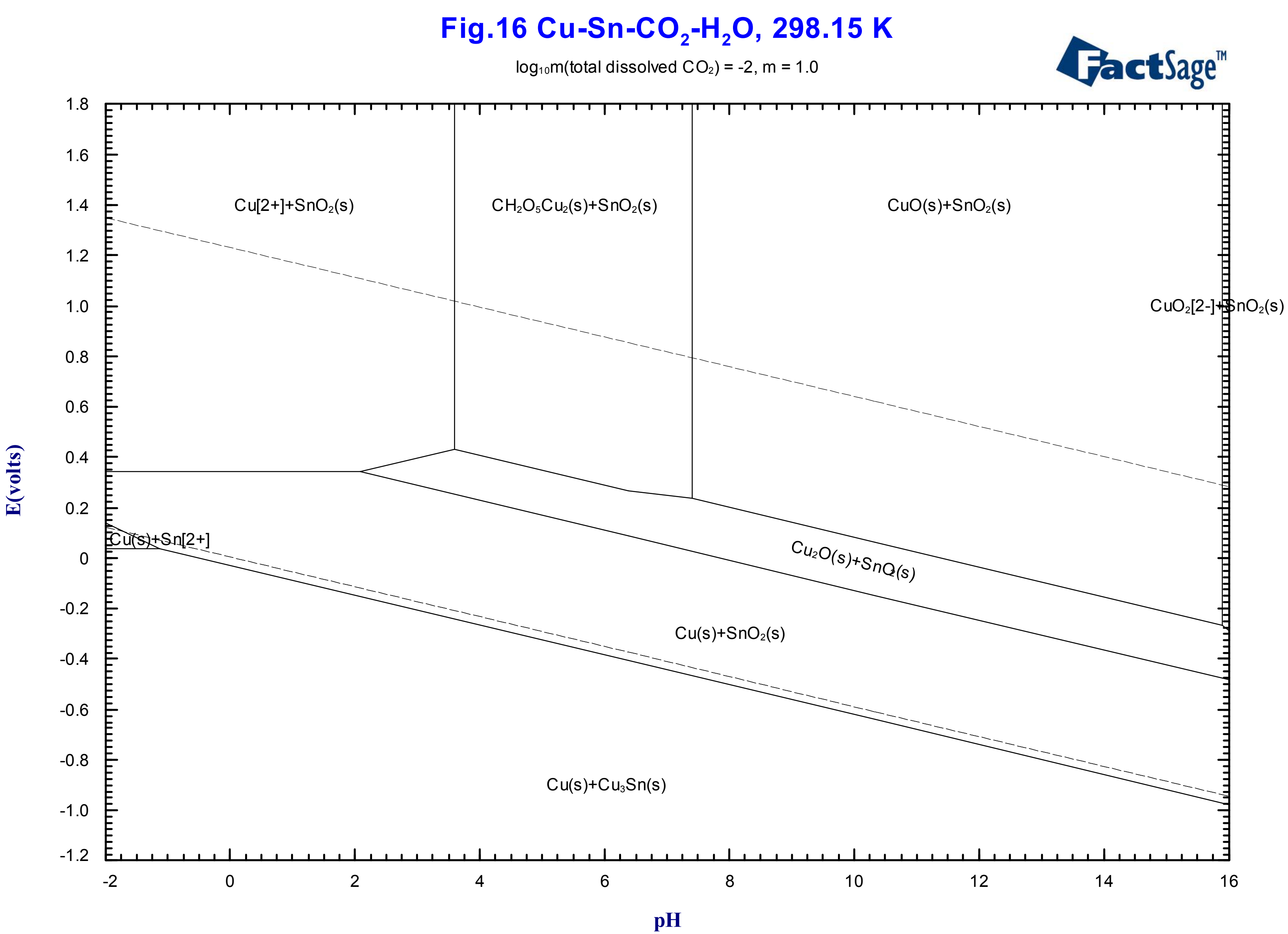


Fig.16 Cu-Sn-CO2-H2O, 298.15 K
log10m(total dissolved CO2) = -2, m = 1.0
FactSage™
Cu[2+]+SnO2(s)
CH2O5Cu2(s)+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

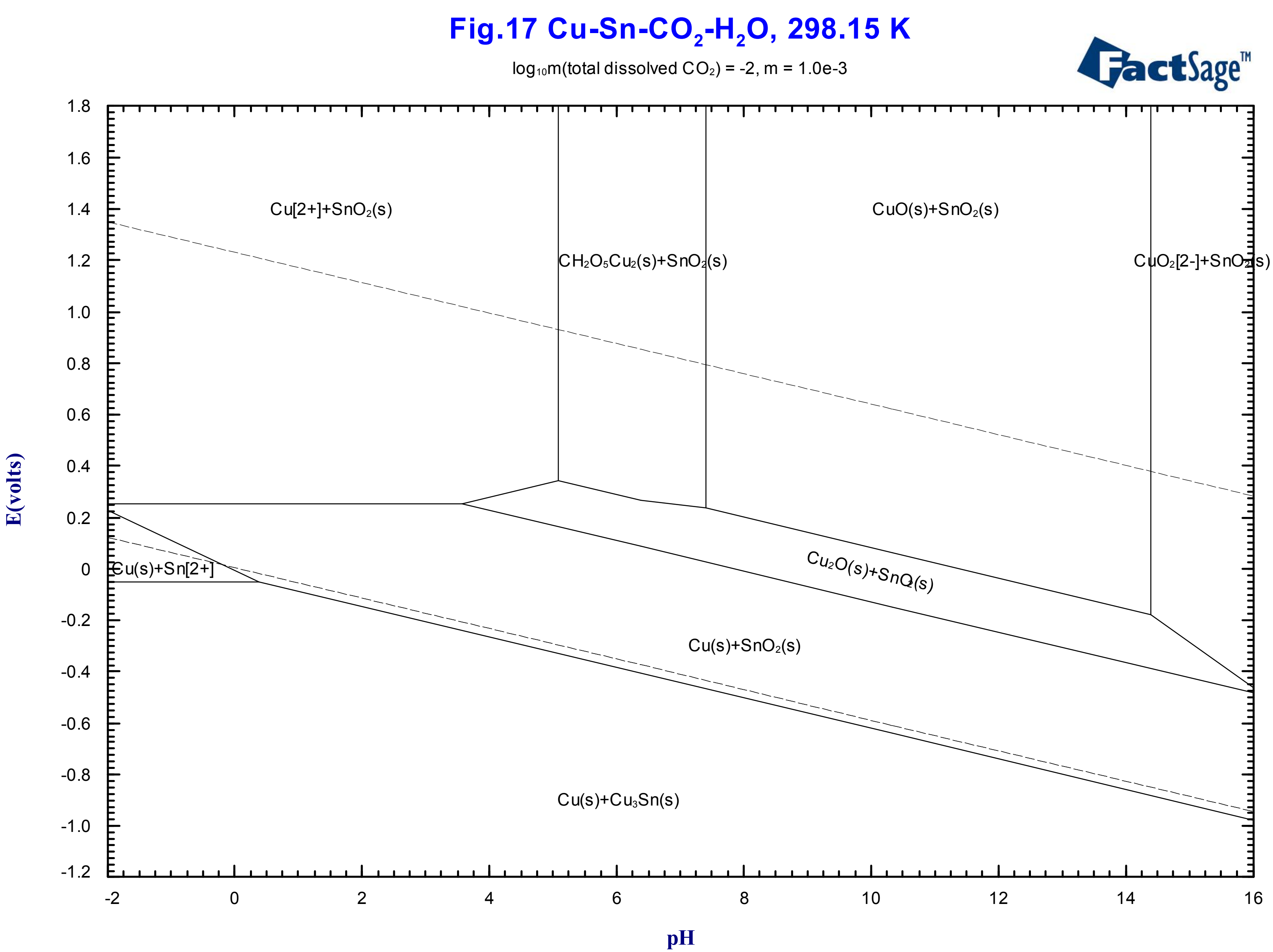


Fig.17 Cu-Sn-CO2-H2O, 298.15 K
log10m(total dissolved CO2) = -2, m = 1.0e-3
FactSage™
Cu[2+]+SnO2(s)
CuO(s)+SnO2(s)
CH2O5Cu2(s)+SnO2(s)
CuO2[2-]+SnO2(s)
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

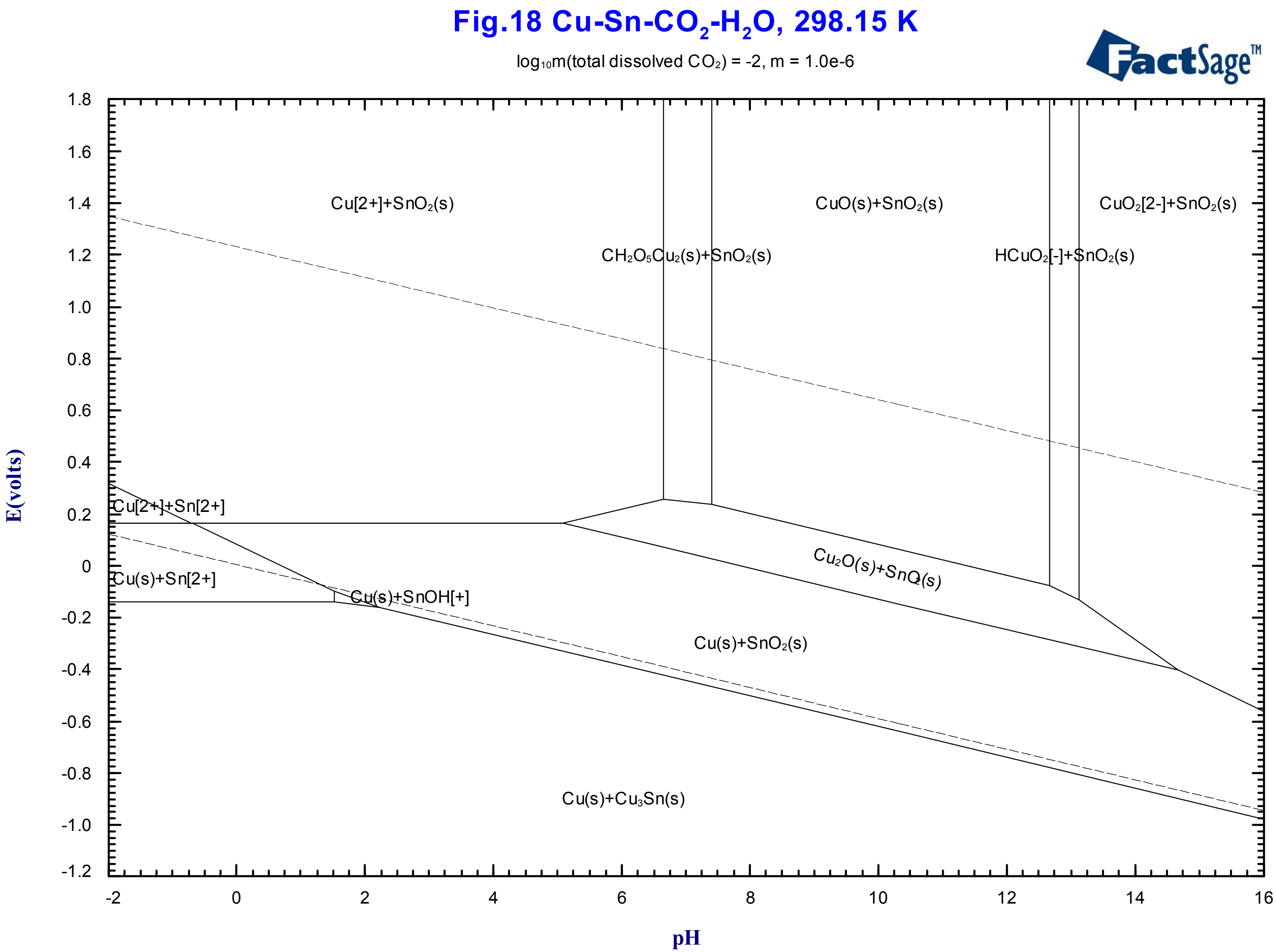


Fig.18 Cu-Sn-CO2-H2O, 298.15 K
log10m(total dissolved CO2) = -2, m = 1.0e-6
Cu[2+]+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
CH2O5Cu2(s)+SnO2(s)
HCuO2[-]+SnO2(s)
Cu[2+]+Sn[2+]
Cu(s)+Sn[2+]
Cu(s)+SnOH[+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

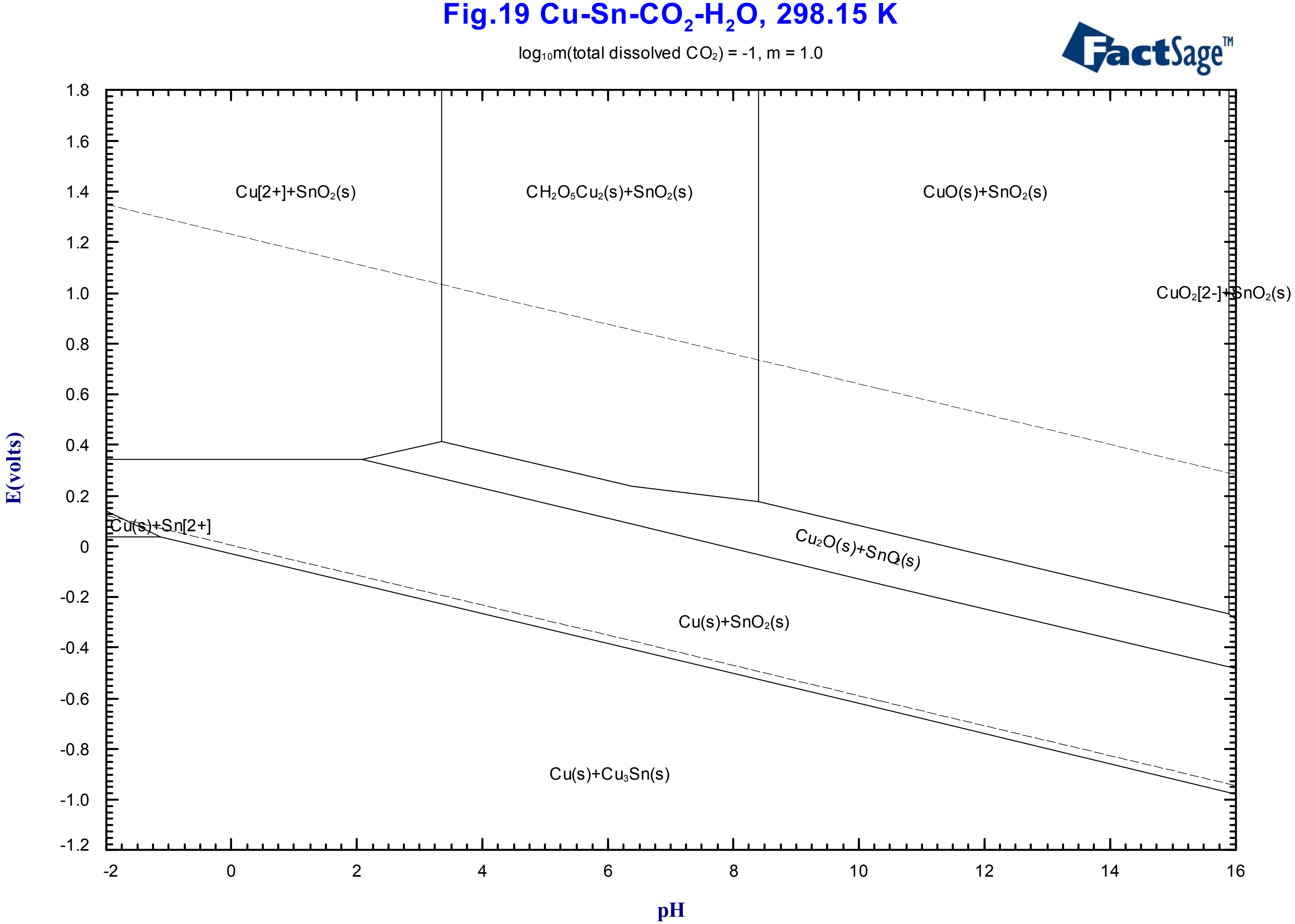


Fig.19 Cu-Sn-CO2-H2O, 298.15 K
log10m(total dissolved CO2) = -1, m = 1.0
Cu[2+]+SnO2(s)
CH2O5Cu2(s)+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

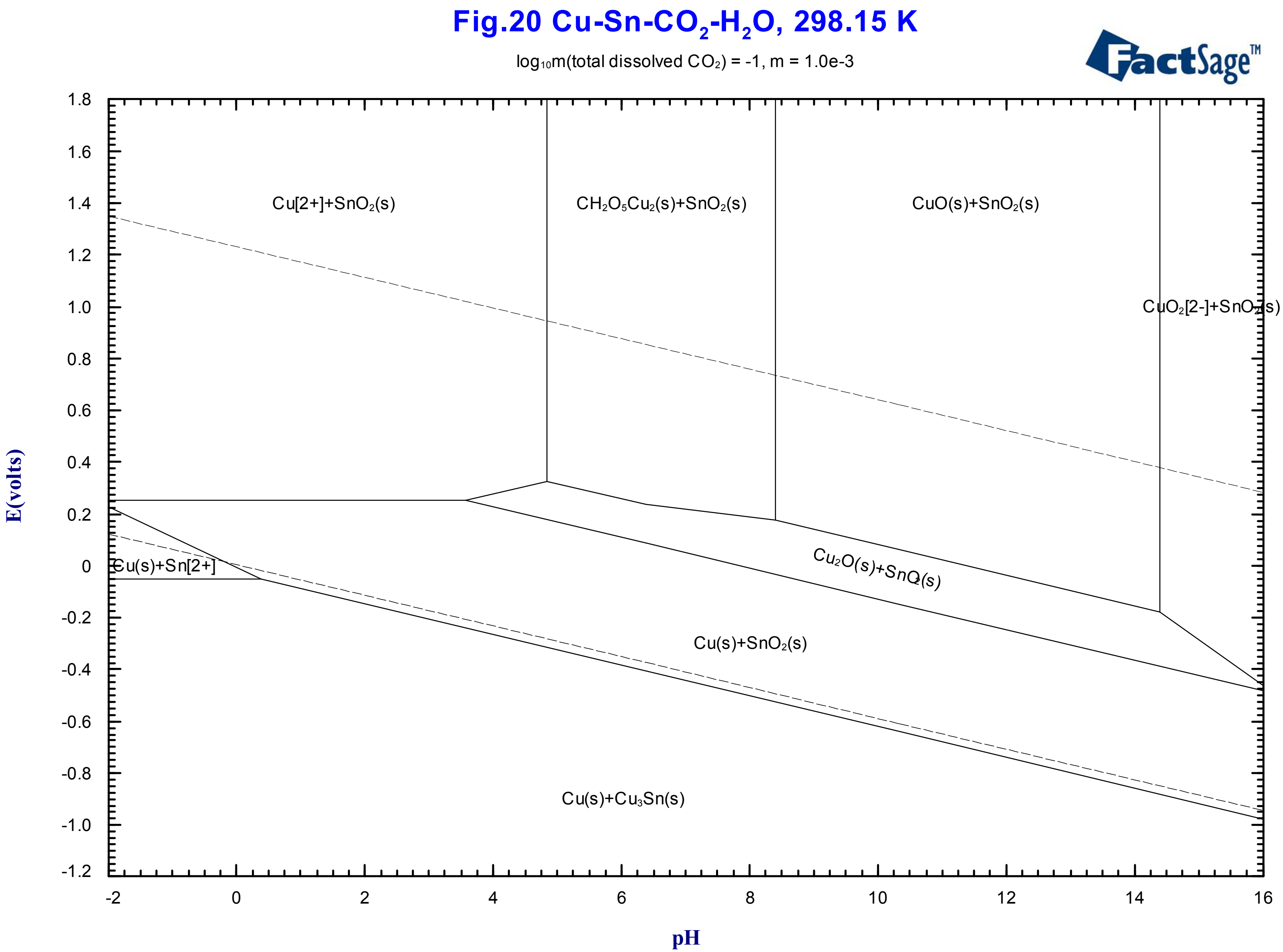
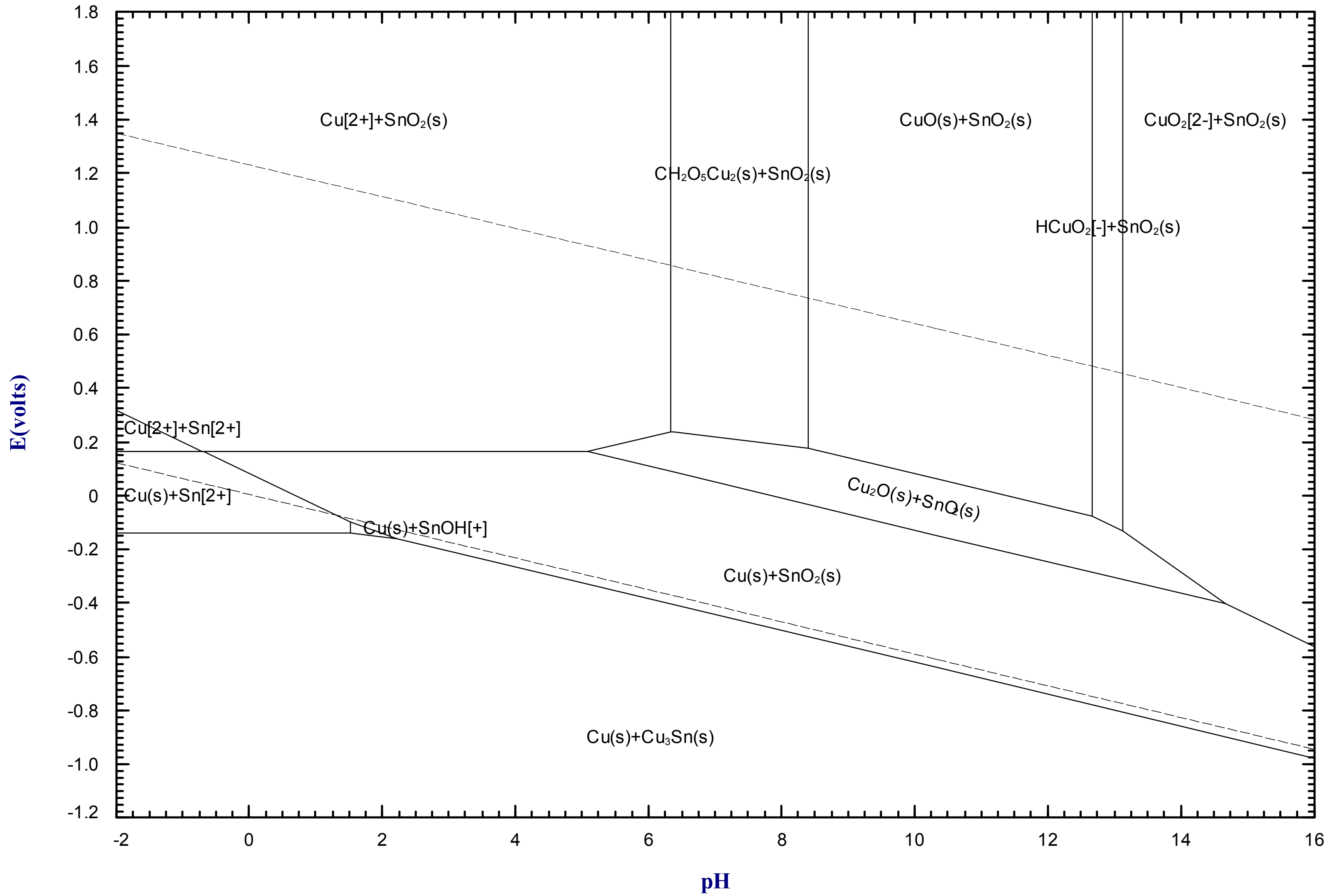


Fig.20 Cu-Sn-CO2-H2O, 298.15 K
log10m(total dissolved CO2) = -1, m = 1.0e-3
FactSage™
Cu[2+]+SnO2(s)
CH2O5Cu2(s)+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
Cu2O(s)+SnO2(s)
Cu(s)+Sn[2+]
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

Fig.21 $Cu-Sn-CO_2-H_2O$, 298.15 K

$log_{10}m$(total dissolved CO_2) = -1, m = 1.0e-6



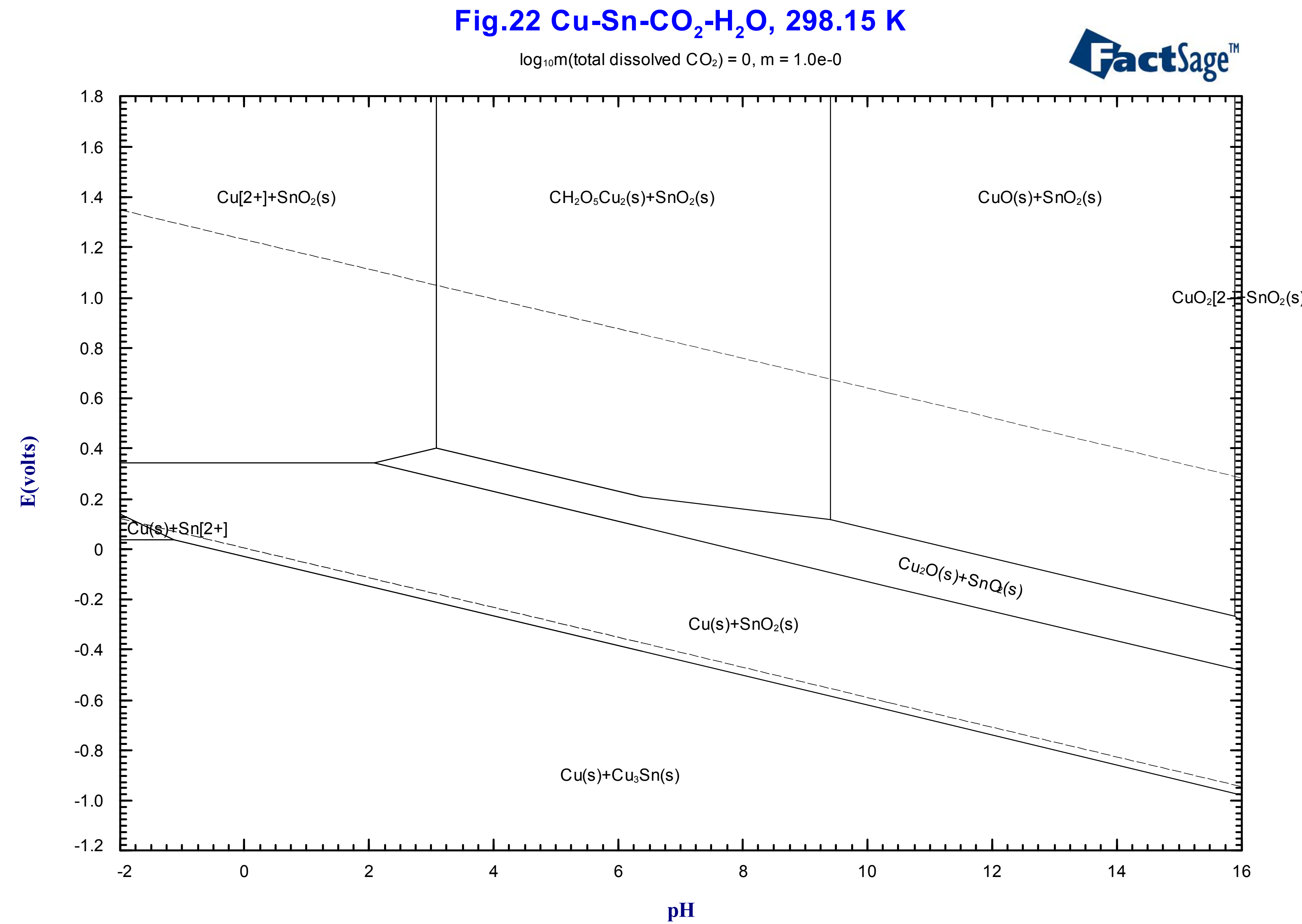
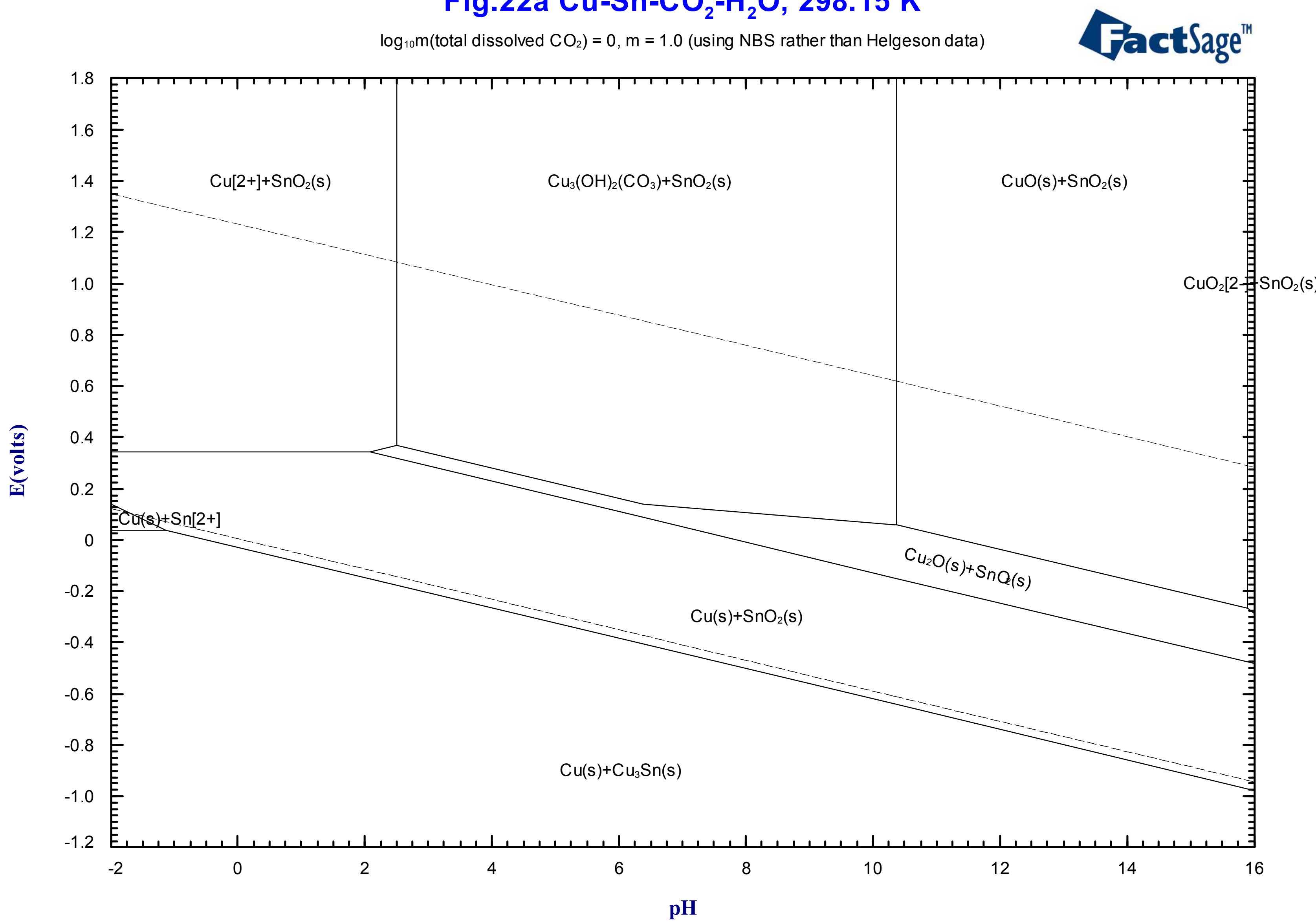


Fig.22 Cu-Sn-CO2-H2O, 298.15 K
log10m(total dissolved CO2) = 0, m = 1.0e-0
FactSage™
Cu[2+]+SnO2(s)
CH2O5Cu2(s)+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

Fig.22a Cu-Sn-CO_2-H_2O, 298.15 K

log_{10}m(total dissolved CO_2) = 0, m = 1.0 (using NBS rather than Helgeson data)



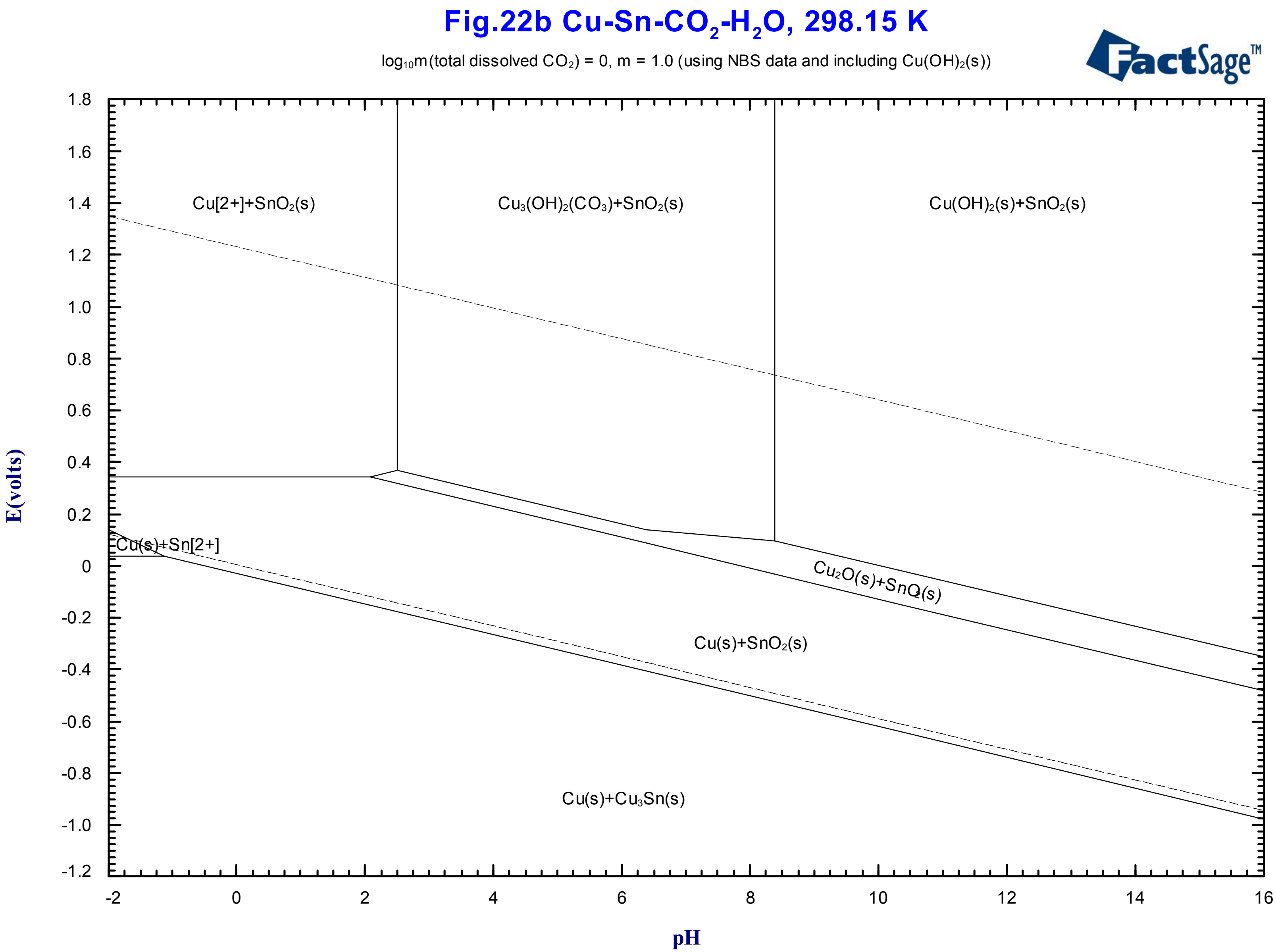


Fig.22b Cu-Sn-CO2-H2O, 298.15 K
log10m(total dissolved CO2) = 0, m = 1.0 (using NBS data and including Cu(OH)2(s))
FactSage™
Cu[2+]+SnO2(s)
Cu3(OH)2(CO3)+SnO2(s)
Cu(OH)2(s)+SnO2(s)
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

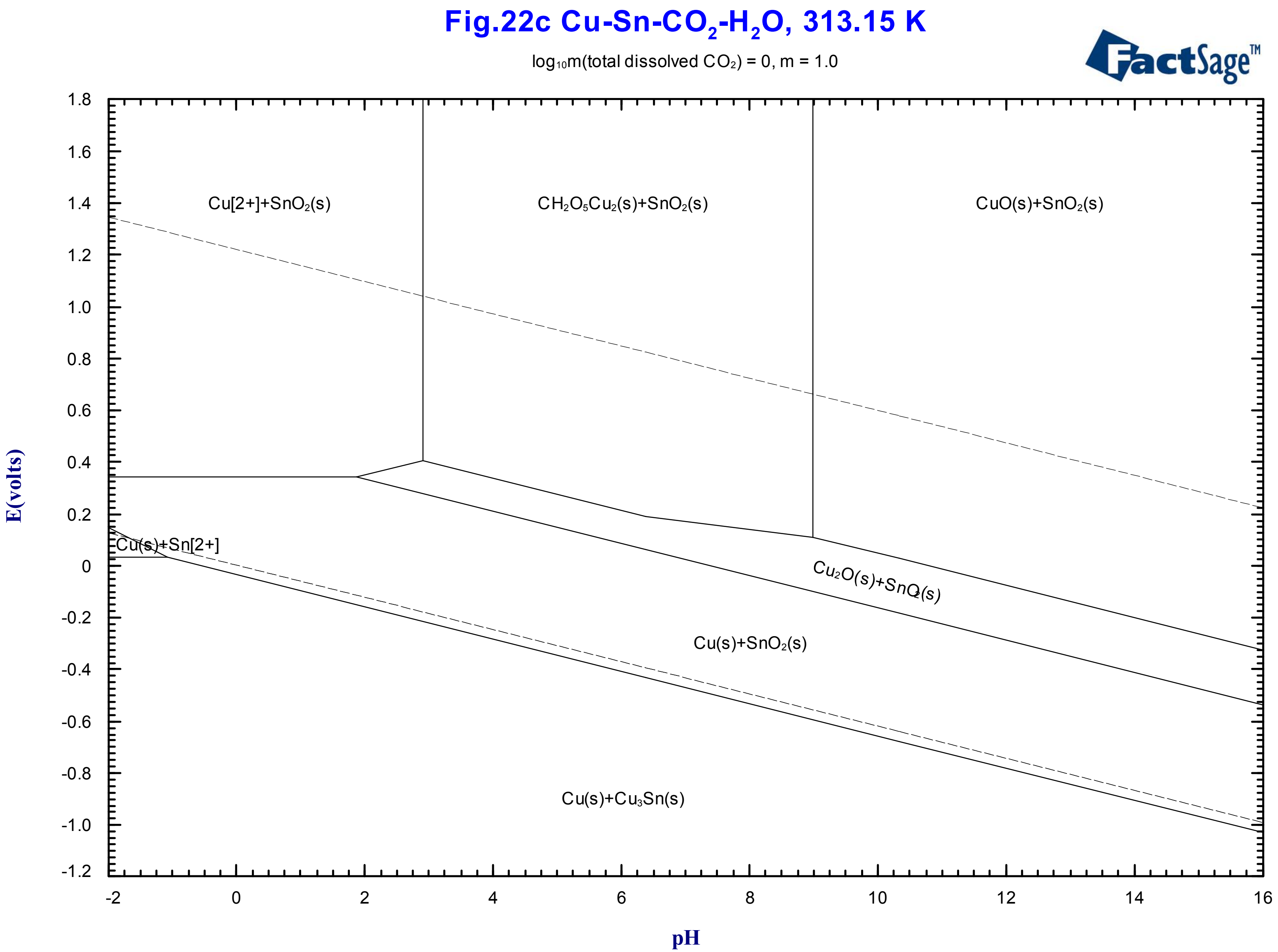


Fig.22c Cu-Sn-CO2-H2O, 313.15 K
log10m(total dissolved CO2) = 0, m = 1.0
FactSage™
Cu[2+]+SnO2(s)
CH2O5Cu2(s)+SnO2(s)
CuO(s)+SnO2(s)
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16

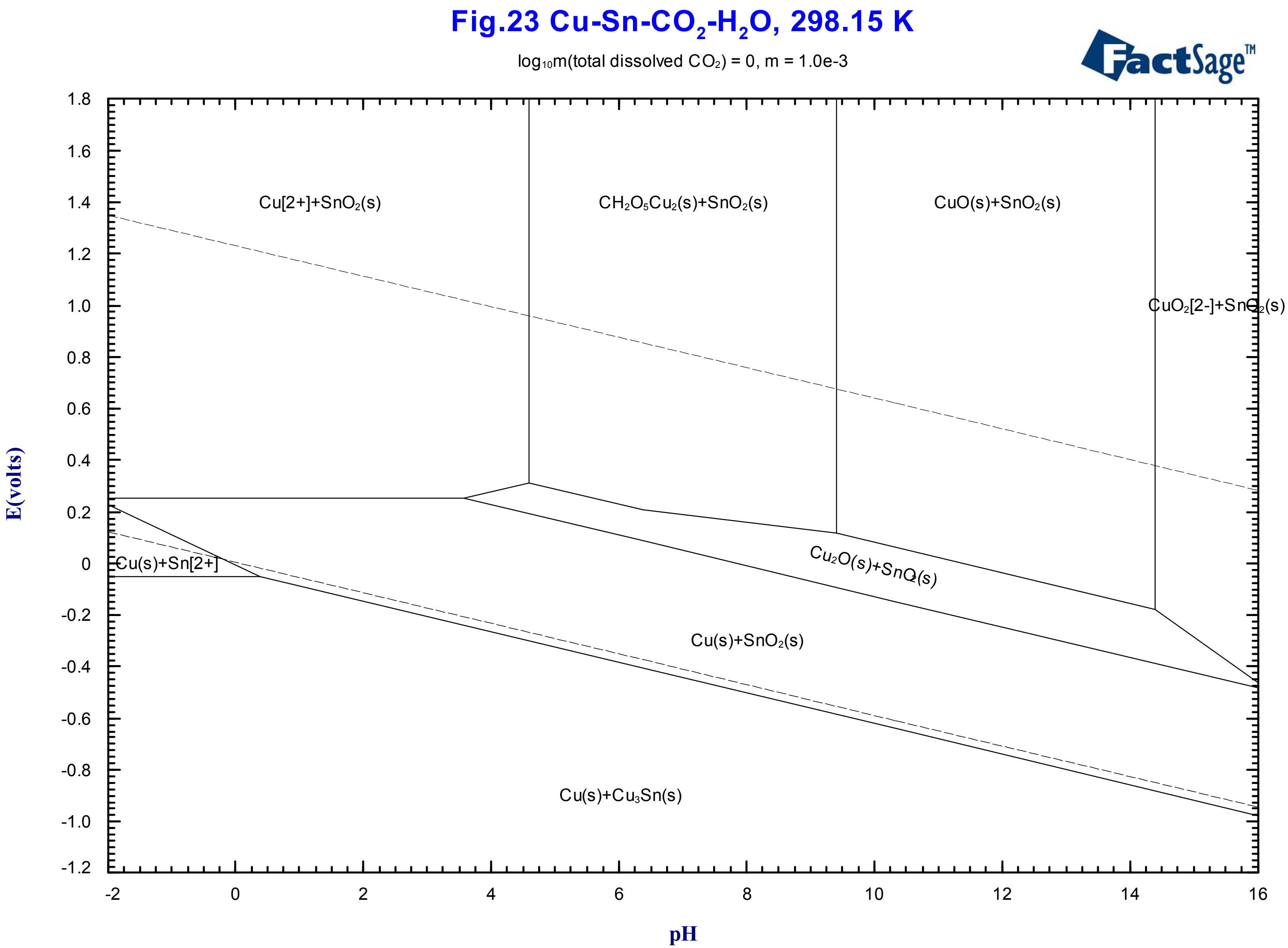


Fig.23 Cu-Sn-CO2-H2O, 298.15 K
log10m(total dissolved CO2) = 0, m = 1.0e-3
Cu[2+]+SnO2(s)
CH2O5Cu2(s)+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
Cu(s)+Sn[2+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH

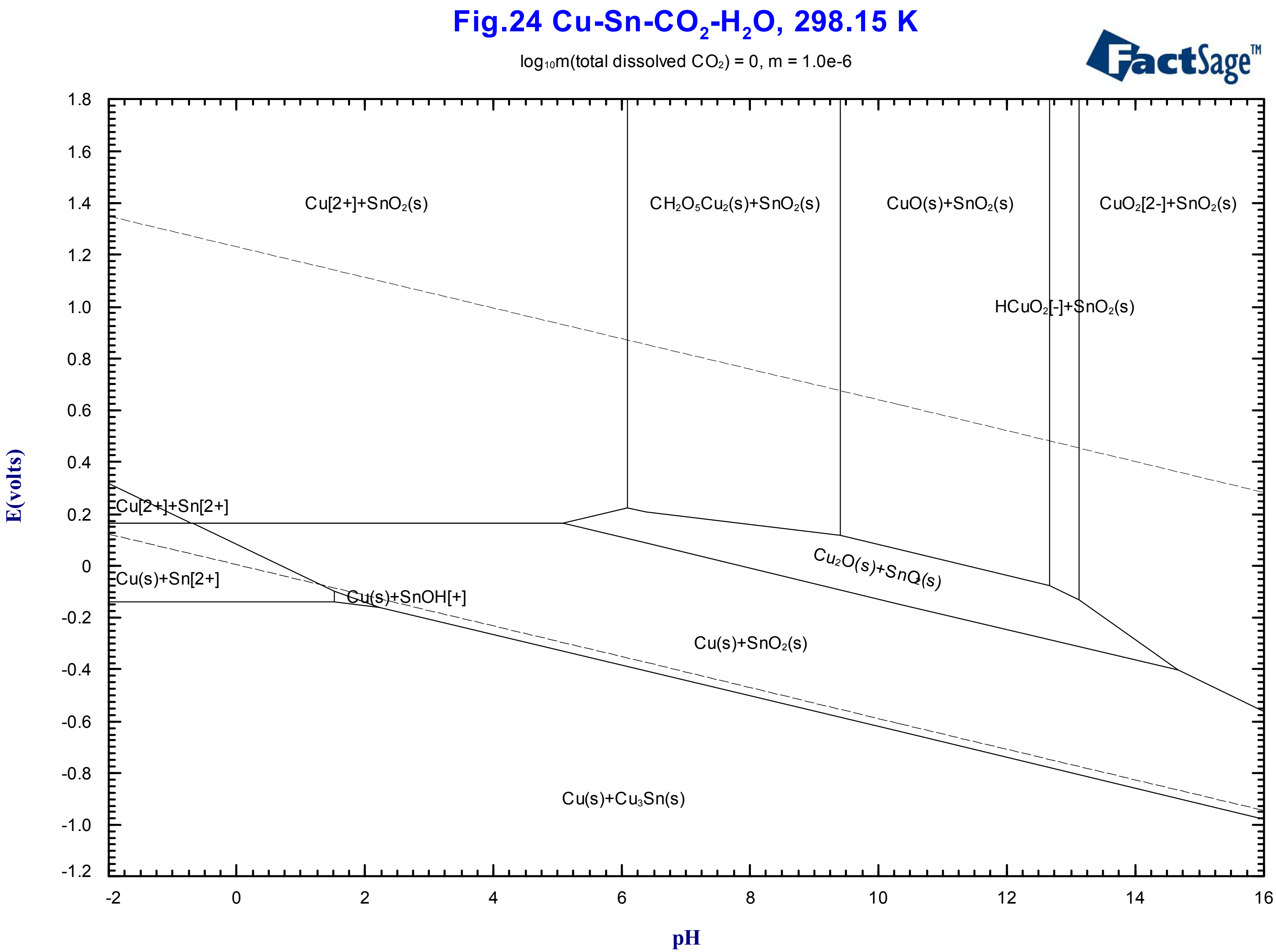


Fig.24 Cu-Sn-CO2-H2O, 298.15 K
log10m(total dissolved CO2) = 0, m = 1.0e-6
FactSage™
Cu[2+]+SnO2(s)
CH2O5Cu2(s)+SnO2(s)
CuO(s)+SnO2(s)
CuO2[2-]+SnO2(s)
HCuO2[-]+SnO2(s)
Cu[2+]+Sn[2+]
Cu(s)+Sn[2+]
Cu(s)+SnOH[+]
Cu2O(s)+SnO2(s)
Cu(s)+SnO2(s)
Cu(s)+Cu3Sn(s)
E(volts)
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-2
0
2
4
6
8
10
12
14
16