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Pictorial Representation of Solid-Gas Equilibria at High Temperatures

Girish Harshé

A pictorial representation of solid-gas equilibria is useful for studying the thermodynamics of a system under consideration. These diagrams show the stability regions of the species involved in a system as functions of pressures of two reacting gases. A computer program initially developed to plot the predominance area diagrams for metal-sulfur-oxygen (M-S-O) systems in roasting processes has been modified and generalized to handle any solid-gas system. This program has been utilized to plot the predominance area diagrams (PAD) for metal-sulfur-oxygen and metal-oxygen systems. The only data input required by the computer are the standard free energy values of all species existing in a system.

Using these diagrams, the optimum pressures of the reacting gases can be determined easily to form the desired species that are stable under these pressure conditions. The computer program may prove to be an important tool for studying thermodynamics of solid-gas systems in different processes like sulfidization roasting, chloridization roasting, volatilization roasting, direct reduction processes in sponge iron manufacturing, high-temperature oxidation, chemical vapor deposition, and reaction sintering of ceramics.

1 Introduction

THE predominance area diagram (PAD) for a system at a given temperature is a plot showing the predominance of the species existing in the system as a function of pressures of the reacting gases in the system. It is also known as a phase stability diagram. The predominance of various species is determined by thermodynamic considerations, namely by comparing the free energy changes associated with different chemical reactions under equilibrium condition.[1] Because the thermodynamic data are available for many compounds[2-4] at different temperatures, these diagrams can be plotted for many systems of interest and can be used in actual applications involving these systems.

To avoid the complications involved in the manual construction of these diagrams, a computer program was developed[5] to plot such diagrams for M-S-O (metal-sulfur-oxygen) systems. The PADs for M-S-O systems are useful in studying the roasting processes involving metal sulfides[6] and high-temperature corrosion of metals in sulfur atmosphere.[7] Because the PADs for M-O (metal-oxygen) systems are also useful in many other processes,[8] this program was modified to plot the PADs for any solid-gas system with at least two reacting gases, the logarithmic pressures of which are the coordinates of these diagrams.

The manual construction of PADs involves many lengthy calculations and hence is a time-consuming and laborious process. To reduce the complexity of manual construction, it becomes necessary to limit the number of species to be considered and to use the practical knowledge of these systems to choose the species. To study the temperature dependence of relative stabilities of the species, PADs at various temperatures are required, which makes the task more difficult. This results in restricting the usage and application of these diagrams, which may be otherwise useful in many industrial processes. The computer program may prove to be useful in overcoming these hurdles and may make it possible to plot PADs for more and more processes. This program can plot these diagrams at various temperatures for any system with no limit on the number of species involved. Thus, using this program, the thermodynamic stability of different species in any system over any range of pressures of the reacting gases and at any temperature can be studied. Using these diagrams, the optimum pressures of the reacting gases and temperature of operation for a process can be determined.

The PADs may be used to study the thermodynamics of sulfidization roasting, chloridization roasting, volatilization roasting, sponge iron production by direct reduction, high-temperature oxidation of metals, reaction sintering of ceramics, and chemical vapor deposition. This paper describes application of the computer program to obtain the PADs for Cu-S-O, Fe-S-O, Co-S-O, Mg-O, and Si-O and briefly discusses the results. A word of caution: The reliability of the PADs mainly depends on the reliability of the thermodynamic data, which vary from source to source.

2 Thermodynamics of Solid-Gas Reactions

A typical solid-gas reaction involving solids S_1, S_2 and gases G_1, G_2 can be expressed in an elementary manner as follows:

$$S_1 + mG_1 \rightarrow qS_2 + nG_2 \text{ Free energy change} = \Delta G^0 \qquad [1]$$

where m, n, and q are the numbers of molecules of G_1, S_2, and G_2, respectively. Hence, the equilibrium constant for this reaction can be written as:

$$K = (pG_2)^n/(pG_1)^m \qquad [2]$$

However, the free energy change is

$$\Delta G^0 = -2.303\,RT \log K \qquad [3]$$

where R is the gas constant, and T is the temperature in Kelvin. Thus, from Eq 2 and 3, one obtains:

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Table 1 Computer Output Listing the Input Data for the Cu-S-O System

```
 No.  Species      No. of Atoms of         Standard Free Energy      Symbol
                  Metal Oxygen Other      G0=A+BTLogT+CT (cal)
                                         (A)          (B)         (C)
-----------------------------------------------------------------------------
 Reacting Gases

( 1) O2          0.     2.     0.           .000        .000        .000

( 2) SO2         0.     2.     1.    -125245.000        .000      32.160
-----------------------------------------------------------------------------
( 1) Cu          1.     0.     0.           .000        .000        .000  1

( 2) CuO         1.     1.     0.     -37725.000      -5.010      36.900  2

( 3) Cu2O        2.     1.     0.     -40500.000      -3.920      29.500  3

( 4) CuS         1.     0.     1.     -67000.000      -3.110      42.720  4

( 5) Cu2S        2.     0.     1.     -72775.000      -6.220      43.590  5

( 6) CuSO4       1.     4.     1.    -221625.000        .000     103.250  6

( 7) CuO.CuSO4   2.     5.     1.    -273205.000     -13.340     177.420  7
-----------------------------------------------------------------------------

   Max-pG2   Min-pG2   Max-pG1   Min-pG1  (atm)

   0.1E+11   0.1E-09   0.1E+03   0.1E-22

-----------------------------------------------------------------------------
```

$$-\Delta G^0/2.303\,RT = n \log (pG_2) - m \log (pG_1) \qquad [4]$$

A plot of this equation with $\log (pG_1)$ as x-axis and $\log (pG_2)$ as y-axis will give a straight line, because the left side of this equation is a constant quantity at a given temperature. When all such reactions of formation for the species involved in a system are obtained as a linear function of the logarithmic pressures of G_1 and G_2, a PAD can be plotted by finding out the most stable species at given pressures of G_1 and G_2.

One can see that if there are N species involved in a system, the number of such straight lines is equal to the number of equilibrium reactions, which is given by $[N(N-1)/2]$. Hence, the construction of PADs for a system involving a large number of species, considering the calculations involved and the time required to do this manually, becomes too complicated. Consequently, the computer program described here simplifies the work and does not put any limit on the number of species to be considered.

3 Computer Program

The computer program, initially developed to plot the PADs for M-S-O systems,[5] was able to plot these diagrams only for the reacting gases SO_2 and O_2. To study the roasting processes for sulfides in the extraction of metals and the corrosion of metals in the presence of sulfur in chemical industries, the knowledge of PADs for various M-S-O becomes essential. Since such diagrams are useful to study any solid-gas reactions, the computer program was extensively modified to plot the PADs for all solid-gas systems (which may involve pure liquids). The new version of this program can be used to plot the PADs for any oxidation process, chloridization process, volatilization process, or even a reduction process (*e.g.*, using H_2).

The logic of the program may be briefly described as follows. First, the chemical reactions between all the pairs of species S_i and S_j involving only the gases G_1 and G_2 other than the pair of species itself, are needed. The number of such reactions will be $[N(N-1)/2]$, where N is the number of all the species in the system, which may possibly form under different pressure and temperature conditions. These are determined using the basic rules of chemistry. Once these are known, using the values of the standard free energy of formation for the species, the standard free energy change (as a function of temperature, *e.g.*, $A + BT \log T + CT$, where A, B, and C are constants) associated with each of these reactions is calculated.

This is followed by calculations of the $\log K$ values for these reactions at a given temperature, which in turn provide the equations of the straight lines appearing in the PAD. Finally, to plot the PAD, the computer divides the diagram into several points,

Table 2 Computer Output Listing the Chemical Reactions Between All the Species in the Cu-S-O System

```
 No.      Chemical Reactions                              Std. Free Energy Change
                                                          Delta G=A+BTLogT+CT (cal)
                                                          (A)          (B)         (C)
-------------------------------------------------------------------------------------
 ( 1) 1.00(Cu         )+ .50(O2        )=(CuO          )
                                              -37725.000       -5.010      36.900
 ( 2) 2.00(Cu         )+ .50(O2        )=(Cu2O         )
                                              -40500.000       -3.920      29.500
 ( 3) 1.00(Cu         )+1.00(SO2       )=(CuS          )+1.00(O2          )
                                               58245.000       -3.110      10.560
 ( 4) 2.00(Cu         )+1.00(SO2       )=(Cu2S         )+1.00(O2          )
                                               52470.000       -6.220      11.430
 ( 5) 1.00(Cu         )+1.00(SO2       )+1.00(O2          )=(CuSO4        )
                                              -96380.000         .000      71.090
 ( 6) 2.00(Cu         )+1.00(SO2       )+1.50(O2          )=(CuO.CuSO4    )
                                             -147960.000      -13.340     145.260
 ( 7) 2.00(CuO        )=(Cu2O        )+ .50(O2          )
                                               34950.000        6.100     -44.300
 ( 8) 1.00(CuO        )+1.00(SO2       )=(CuS          )+1.50(O2          )
                                               95970.000        1.900     -26.340
 ( 9) 2.00(CuO        )+1.00(SO2       )=(Cu2S         )+2.00(O2          )
                                              127920.000        3.800     -62.370
 (10) 1.00(CuO        )+1.00(SO2       )+ .50(O2          )=(CuSO4        )
                                              -58655.000        5.010      34.190
 (11) 2.00(CuO        )+1.00(SO2       )+ .50(O2          )=(CuO.CuSO4    )
                                              -72510.000       -3.320      71.460
 (12)  .50(Cu2O       )+1.00(SO2       )=(CuS          )+1.25(O2          )
                                               78495.000       -1.150      -4.190
 (13) 1.00(Cu2O       )+1.00(SO2       )=(Cu2S         )+1.50(O2          )
                                               92970.000       -2.300     -18.070
 (14)  .50(Cu2O       )+1.00(SO2       )+ .75(O2          )=(CuSO4        )
                                              -76130.000        1.960      56.340
 (15) 1.00(Cu2O       )+1.00(SO2       )+1.00(O2          )=(CuO.CuSO4    )
                                             -107460.000       -9.420     115.760
 (16) 2.00(CuS        )+1.00(O2        )=(Cu2S         )+1.00(SO2         )
                                              -64020.000         .000      -9.690
 (17) 1.00(CuS        )+2.00(O2        )=(CuSO4        )
                                             -154625.000        3.110      60.530
 (18) 2.00(CuS        )+3.50(O2        )=(CuO.CuSO4    )+1.00(SO2         )
                                             -264450.000       -7.120     124.140
 (19)  .50(Cu2S       )+ .50(SO2       )+1.50(O2          )=(CuSO4        )
                                             -122615.000        3.110      65.375
 (20) 1.00(Cu2S       )+2.50(O2        )=(CuO.CuSO4    )
                                             -200430.000       -7.120     133.830
 (21) 2.00(CuSO4      )=(CuO.CuSO4   )+1.00(SO2         )+ .50(O2          )
                                               44800.000      -13.340       3.080
-------------------------------------------------------------------------------------
```

uses the log K values to compare the stability of the species at each of these points, and finds out the most stable species using the criterion of the most negative free energy change of the reactions. This is carried out line by line for the whole diagram. To mark the predominance region of a species, the computer prints the character symbol of that species at the boundaries of that region. These symbols are fed to the computer as a part of the input. These steps are repeated for various temperatures and for different systems.

3.1 *Input*

A typical input to this program is shown in Table 1. Significant values are the numbers of atoms of different elements and

Table 3 Computer Output Listing the Relations Between the Partial Pressures of SO_2 and O_2 for the Cu-S-O System

```
Temperature =  900.(Kelvin)

Relations between Log(pG2) and Log(pG1) for the above chemical reactions.
-------------------------------------------------------------------------------
( 1)  (      4.333)=(      .000)Log(pG2)+(     -.500)Log(pG1)

( 2)  (      5.921)=(      .000)Log(pG2)+(     -.500)Log(pG1)

( 3)  (    -14.449)=(    -1.000)Log(pG2)+(     1.000)Log(pG1)

( 4)  (    -11.228)=(    -1.000)Log(pG2)+(     1.000)Log(pG1)

( 5)  (      7.870)=(    -1.000)Log(pG2)+(    -1.000)Log(pG1)

( 6)  (     12.801)=(    -1.000)Log(pG2)+(    -1.500)Log(pG1)

( 7)  (     -2.745)=(      .000)Log(pG2)+(      .500)Log(pG1)

( 8)  (    -18.782)=(    -1.000)Log(pG2)+(     1.500)Log(pG1)

( 9)  (    -19.893)=(    -1.000)Log(pG2)+(     2.000)Log(pG1)

(10)  (      3.538)=(    -1.000)Log(pG2)+(     -.500)Log(pG1)

(11)  (      4.135)=(    -1.000)Log(pG2)+(     -.500)Log(pG1)

(12)  (    -17.409)=(    -1.000)Log(pG2)+(     1.250)Log(pG1)

(13)  (    -17.148)=(    -1.000)Log(pG2)+(     1.500)Log(pG1)

(14)  (      4.910)=(    -1.000)Log(pG2)+(     -.750)Log(pG1)

(15)  (      6.880)=(    -1.000)Log(pG2)+(    -1.000)Log(pG1)

(16)  (     17.670)=(     1.000)Log(pG2)+(    -1.000)Log(pG1)

(17)  (     22.319)=(      .000)Log(pG2)+(    -2.000)Log(pG1)

(18)  (     41.699)=(     1.000)Log(pG2)+(    -3.500)Log(pG1)

(19)  (     13.484)=(     -.500)Log(pG2)+(    -1.500)Log(pG1)

(20)  (     24.028)=(      .000)Log(pG2)+(    -2.500)Log(pG1)

(21)  (     -2.940)=(     1.000)Log(pG2)+(      .500)Log(pG1)
-------------------------------------------------------------------------------
```

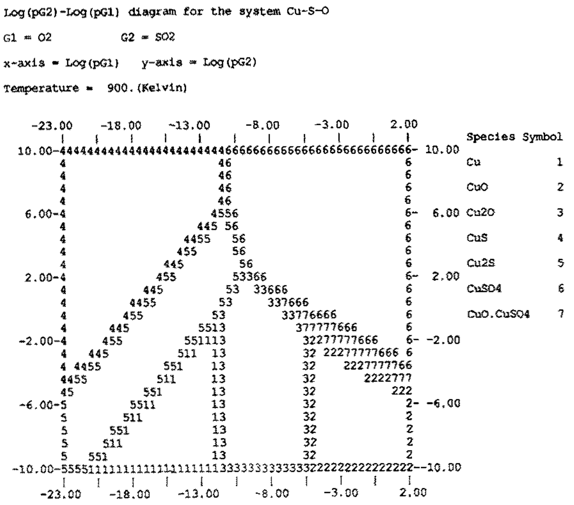
the standard free energies of formation as a function of temperature ($G^0 = A + BT \log T + CT$, cal.) for each of the species.

3.2 *Output*

The output consists of (1) a listing of all the data input (Table 1); (2) all the chemical reactions taking place in the system (Table 2); (3) all the relations between log G_1 and log G_2 for a given temperature, which are also the equations of the straight lines appearing on the PAD (Table 3); and (4) the PAD for the given temperature with the explanation of the symbols (Fig. 1).

4 Results and Discussion

The computer program has been used to plot the PADs for Cu-S-O, Fe-S-O, Co-S-O, Mg-O, and Si-O. These are shown in Fig. 1 through 7. To study the variation of relative stabilities of different species, the PADs at different temperatures for a system must be studied. The stability regions contract or expand without changing the slopes of the boundaries. This is because the variation in temperature does not change the chemical reaction, but it only affects the free energy change associated with the reaction. The slope of a boundary line is determined by the



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Log(pG2)-Log(pG1) diagram for the system Cu-S-O

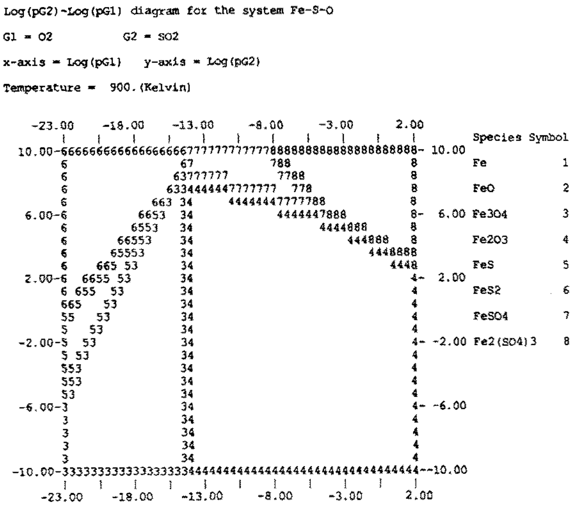
G1 = O2           G2 = SO2

x-axis = Log(pG1)   y-axis = Log(pG2)

Temperature =  900.(Kelvin)

   -23.00    -18.00    -13.00     -8.00     -3.00      2.00
       |    |    |    |    |    |    |    |    |    |    |        Species Symbol
 10.00-444444444444444444444444666666666666666666666666666- 10.00
       4                      46                         6        Cu           1
       4                      46                         6
       4                      46                         6        CuO          2
       4                      46                         6
  6.00-4                     4556                        6-  6.00 Cu2O         3
       4                   445 56                        6
       4                 4455   56                       6        CuS          4
       4                455     56                       6
       4              445        56                      6        Cu2S         5
  2.00-4             455        53366                    6-  2.00
       4           445         53  33666                 6        CuSO4        6
       4         4455         53     337666              6
       4        455          53        33776666          6        CuO.CuSO4    7
       4      445          5513          377777666       6
 -2.00-4     455         551113           32277777666    6- -2.00
       4   445          511  13           32 22277777666 6
       4 4455         551    13           32    2227777766
       4455          511     13           32       2222777
       45          551       13           32           222
 -6.00-5         5511        13           32             2- -6.00
       5        511          13           32             2
       5      551            13           32             2
       5     511             13           32             2
       5   551               13           32             2
-10.00-555511111111111111111113333333333333222222222222222--10.00
       |    |    |    |    |    |    |    |    |    |    |
   -23.00    -18.00    -13.00     -8.00     -3.00      2.00
```

Fig. 1 Computer-plotted predominance area diagram for Cu-S-O system at 900 K.



```
Log(pG2)-Log(pG1) diagram for the system Fe-S-O

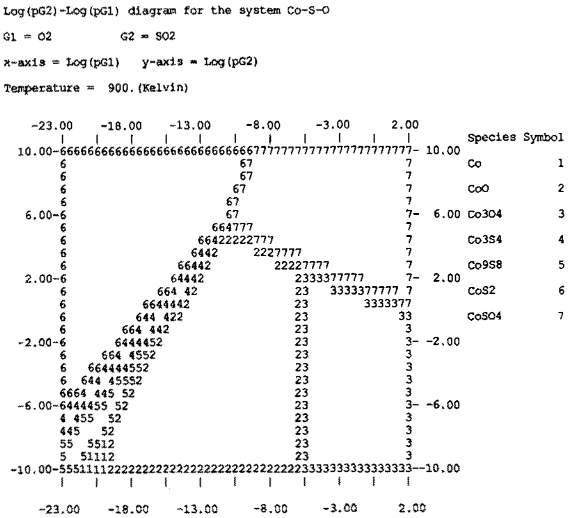
G1 = O2           G2 = SO2

x-axis = Log(pG1)   y-axis = Log(pG2)

Temperature =  900.(Kelvin)

   -23.00    -18.00    -13.00     -8.00     -3.00      2.00
       |    |    |    |    |    |    |    |    |    |    |        Species Symbol
 10.00-666666666666666666777777777777888888888888888888888- 10.00
       6                67           788                 8        Fe           1
       6               63777777       7788               8
       6              6334444447777777  778              8        FeO          2
       6            663 34     44444447777788            8
  6.00-6          6653  34            4444447888         8-  6.00 Fe3O4        3
       6         6553   34                  4444888      8
       6       66553    34                      444888   8        Fe2O3        4
       6      65553     34                         4448888
       6    665 53      34                            4448        FeS          5
  2.00-6  6655 53       34                               4-  2.00
       6 655  53        34                               4        FeS2         6
       665   53         34                               4
       55   53          34                               4        FeSO4        7
       5   53           34                               4
 -2.00-5  53            34                               4- -2.00 Fe2(SO4)3    8
       5 53             34                               4
       553              34                               4
       553              34                               4
       53               34                               4
 -6.00-3                34                               4- -6.00
       3                34                               4
       3                34                               4
       3                34                               4
       3                34                               4
-10.00-333333333333333333444444444444444444444444444444444--10.00
       |    |    |    |    |    |    |    |    |    |    |
   -23.00    -18.00    -13.00     -8.00     -3.00      2.00
```

Fig. 2 Computer-plotted predominance area diagram for Fe-S-O system at 900 K.



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Log(pG2)-Log(pG1) diagram for the system Co-S-O

G1 = O2           G2 = SO2

x-axis = Log(pG1)   y-axis = Log(pG2)

Temperature =  900.(Kelvin)

   -23.00    -18.00    -13.00     -8.00     -3.00      2.00
       |    |    |    |    |    |    |    |    |    |    |        Species Symbol
 10.00-666666666666666666666666666777777777777777777777777- 10.00
       6                         67                      7        Co           1
       6                         67                      7
       6                        67                       7        CoO          2
       6                       67                        7
  6.00-6                       67                        7-  6.00 Co3O4        3
       6                     664777                      7
       6                   66422222777                   7        Co3S4        4
       6                  6442     2227777               7
       6                66442         22227777           7        Co9S8        5
  2.00-6               64442             2333377777      7-  2.00
       6             664 42              23   3333377777 7        CoS2         6
       6           6644442               23        3333377
       6          644 422                23             33        CoSO4        7
       6        664 442                  23              3
 -2.00-6       6444452                   23              3- -2.00
       6     664 4552                    23              3
       6   664444552                     23              3
       6  644 45552                      23              3
       6664 445 52                       23              3
 -6.00-6444455 52                        23              3- -6.00
       4 455  52                         23              3
       445   52                          23              3
       55  5512                          23              3
       5  51112                          23              3
-10.00-555111222222222222222222222222222223333333333333333--10.00
       |    |    |    |    |    |    |    |    |    |    |

   -23.00    -18.00    -13.00     -8.00     -3.00      2.00
```
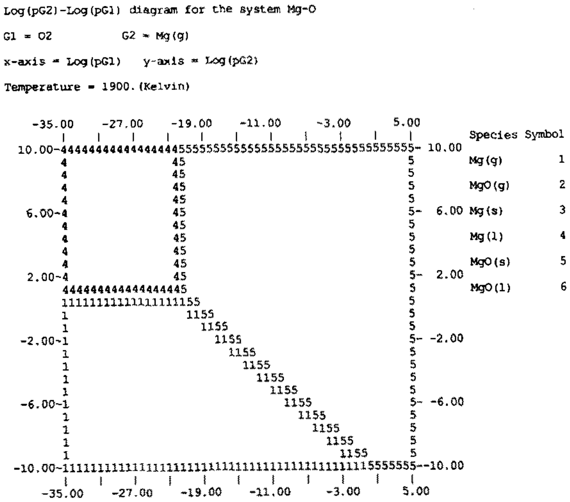

Fig. 3 Computer-plotted predominance area diagram for Co-S-O system at 900 K.



```
Log(pG2)-Log(pG1) diagram for the system Mg-O

G1 = O2           G2 = Mg(g)

x-axis = Log(pG1)   y-axis = Log(pG2)

Temperature = 1900.(Kelvin)

   -35.00    -27.00    -19.00    -11.00     -3.00      5.00
       |    |    |    |    |    |    |    |    |    |    |        Species Symbol
 10.00-444444444444444445555555555555555555555555555555555- 10.00
       4               45                                5        Mg(g)        1
       4               45                                5
       4               45                                5        MgO(g)       2
       4               45                                5
  6.00-4               45                                5-  6.00 Mg(s)        3
       4               45                                5
       4               45                                5        Mg(l)        4
       4               45                                5
       4               45                                5        MgO(s)       5
  2.00-4               45                                5-  2.00
       444444444444444445                                5        MgO(l)       6
       11111111111111111155                              5
       1                 1155                            5
       1                   1155                          5
 -2.00-1                     1155                        5- -2.00
       1                       1155                      5
       1                         1155                    5
       1                           1155                  5
       1                             1155                5
 -6.00-1                               1155              5- -6.00
       1                                 1155            5
       1                                   1155          5
       1                                     1155        5
       1                                       1155      5
-10.00-111111111111111111111111111111111111111111115555555--10.00
       |    |    |    |    |    |    |    |    |    |    |
   -35.00    -27.00    -19.00    -11.00     -3.00      5.00
```

Fig. 4 Computer-plotted predominance area diagram for Mg-O system at 1900 K.

ratio of the numbers of the molecules of the gases reacting together to form one species from another, which remains unchanged.

4.1 *M-S-O Systems*

Figures 1, 2, and 3 show the PADs for Cu-S-O, Fe-S-O, and Co-S-O at 900 K. These PADs are useful when dealing with a single system, or with a mixture of two or more systems. The latter is often true in extractive metallurgy where the ore is always a mixture of two or more systems. For example, when copper ore is to be processed, the impurities containing iron sulfides and possibly cobalt sulfides should be separated. If the ore is treated in such a manner that copper gets converted to copper sulfate, whereas iron and cobalt get converted to water-insoluble oxides, they can be separated easily by dissolving copper sulfate in water. The copper sulfate solution can be further processed by a hydrometallurgical route to produce fine copper powder in an autoclave by hydrogen reduction. The ore treatment required is necessarily an oxidation roasting process, in which the oxygen pressure and temperature is controlled so that the process yields the desired products. The optimum pressure and temperature values can be obtained by superimposing the PADs of Cu-S-O, Fe-S-O, and Co-S-O and then finding the pressure ranges of O_2

```
Log(pG2)-Log(pG1) diagram for the system MgO-O

G1 = O2            G2 = MgO(g)

x-axis = Log(pG1)   y-axis = Log(pG2)

Temperature = 1900.(Kelvin)

    -35.00    -27.00    -19.00    -11.00     -3.00     5.00
       |    |    |    |    |    |    |    |    |    |    |        Species Symbol
 10.00-2222222222222222222555555555555555555555555555555555- 10.00
       2                 25                              5        MgO(g)          1
       2                 25                              5
       2                 25                              5        Mg(g)           2
       2                 25                              5
  6.00-2                 25                              5-  6.00 Mg(s)           3
       2                 25                              5
       2                 25                              5        Mg(l)           4
       2                 25                              5
       2                 25                              5        MgO(s)          5
  2.00-2                 25                              5-  2.00
       2                 25                              5        MgO(l)          6
       2                 25                              5
       2                 25                              5
       2                 25                              5
 -2.00-2                 25                              5- -2.00
       2                 25                              5
       2                 25                              5
       2                 25                              5
       2                 25                              5
 -6.00-2                 25                              5- -6.00
       2                 255555555555555555555555555555555
       2               22111111111111111111111111111111111
       2             2211                                1
       2           2211                                  1
-10.00-222222222222111111111111111111111111111111111111111--10.00
       |    |    |    |    |    |    |    |    |    |    |
    -35.00    -27.00    -19.00    -11.00     -3.00     5.00
```

Fig. 5 Computer-plotted predominance area diagram for MgO-O system at 1900 K.

```
Log(pG2)-Log(pG1) diagram for the system Si-O

G1 = O2            G2 = Si(g)

x-axis = Log(pG1)   y-axis = Log(pG2)

Temperature = 1900.(Kelvin)

    -20.00    -15.00    -10.00     -5.00      .00     5.00
       |    |    |    |    |    |    |    |    |    |    |        Species Symbol
 10.00-333333333335555555555555555555555555555555555555555- 10.00
       3         35                                      5        Si(g)           4
       3         35                                      5
       3         35                                      5        SiO(g)          1
       3         35                                      5
  6.00-3         35                                      5-  6.00 Si(s)           2
       3         35                                      5
       3         35                                      5        Si(l)           3
       3         35                                      5
       3         35                                      5        SiO2(s)         5
  2.00-3         35                                      5-  2.00
       3         35                                      5        SiO2(l)         6
       3         35                                      5
       3         35                                      5
       3         35                                      5
 -2.00-3         35                                      5- -2.00
       3         35                                      5
       333333333335                                      5
       44444444444455                                    5
       4           445                                   5
 -6.00-4             455                                 5- -6.00
       4              4455                               5
       4                445                              5
       4                  455                            5
       4                   445                           5
-10.00-444444444444444444444455555555555555555555555555555--10.00
       |    |    |    |    |    |    |    |    |    |    |
    -20.00    -15.00    -10.00     -5.00      .00     5.00
```

Fig. 6 Computer-plotted predominance area diagram for Si-O system at 1900 K.

```
Log(pG2)-Log(pG1) diagram for the system SiO-O

G1 = O2            G2 = SiO(g)

x-axis = Log(pG1)   y-axis = Log(pG2)

Temperature = 1900.(Kelvin)

    -20.00    -15.00    -10.00     -5.00      .00     5.00
       |    |    |    |    |    |    |    |    |    |    |        Species Symbol
 10.00-333333333335555555555555555555555555555555555555555- 10.00
       3         35                                      5        SiO(g)          1
       3         35                                      5
       3         35                                      5        Si(s)           2
       3         35                                      5
  6.00-3         35                                      5-  6.00 Si(l)           3
       3         35                                      5
       3         35                                      5        Si(g)           4
       3         35                                      5
       3         35                                      5        SiO2(s)         5
  2.00-3         35                                      5-  2.00
       3         35                                      5        SiO2(l)         6
       3         35                                      5
       3        3355                                     5
       3     3331111555                                  5
 -2.00-3  333111    111555                               5- -2.00
       333111          111555                            5
       111                111555                         5
       1                     1115555                     5
       1                        1111555                  5
 -6.00-1                            111555               5- -6.00
       1                               111555            5
       1                                  111555         5
       1                                     1115555     5
       1                                        1111555  5
-10.00-111111111111111111111111111111111111111111111111555--10.00
       |    |    |    |    |    |    |    |    |    |    |
    -20.00    -15.00    -10.00     -5.00      .00     5.00
```

Fig. 7 Computer-plotted predominance area diagram for SiO-O system at 1900 K.

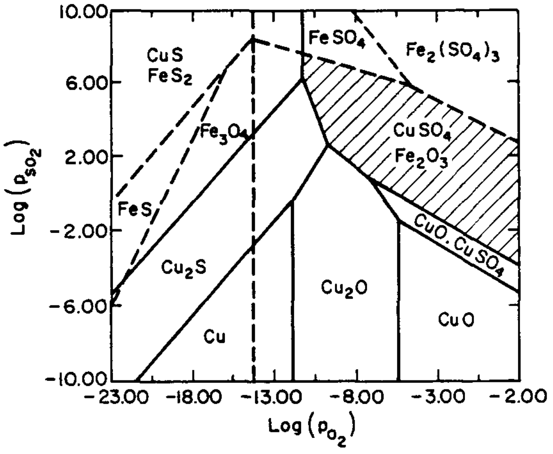


Fig. 8 Superimposed predominance area diagrams for Cu-S-O and Fe-S-O system at 900 K.

and SO_2 where copper sulfate, iron oxides, and cobalt oxides coexist. This method can be repeated to separate iron and cobalt.

The procedure can be best illustrated by an example of the separation of copper and iron. Figure 8 shows the superimposed PADs of Cu-S-O and Fe-S-O at 900 K. If the pressures of O_2 and SO_2 are maintained at the values corresponding to the shaded region, the roasting process will yield $CuSO_4$ and Fe_2O_3. The products can be further treated with water to separate soluble $CuSO_4$ and insoluble Fe_2O_3.

In a highly corrosive atmosphere, the effect of sulfur on the corrosion of Fe can be studied using these diagrams. Such diagrams can also be plotted for other metal-sulfur-oxygen systems to study the corrosion resistance of those metals.

4.2 *M-O Systems*

In this system, two different PADs are possible, because the *y*-axis can represent either the partial pressure of metal or the partial pressure of metal oxide. Figure 4 shows the PAD with Mg and O_2 pressures as the coordinates and Fig. 5 shows the PAD with MgO and O_2 pressures as the coordinates, for the system Mg-O at 1900 K . Figure 6 shows the PAD with Si and O_2 pressures as the coordinates, and Fig. 7 shows the PAD with SiO and O_2 pressures as the coordinates, for the system Si-O at 1900 K.

These PADs are useful in sintering of MgO and SiO_2. One can study the formation of high-temperature phases at different vapor pressures of Mg or Si. These diagrams can be applied to reaction sintering of ceramics in synthesis of ceramics (*e.g.*, a PAD for Si-N can be used in the synthesis of Si_3N_4).

5 Conclusion

A computer program has been developed that can plot the predominance area diagrams for any solid-gas system at different temperatures of reactions. These diagrams are useful in studying the thermodynamics of solid-gas reactions at high temperatures, to obtain the optimum pressures of the reacting gases, and the optimum temperature of the process to obtain the desired reaction products. The PADs plotted using this program can be applied to many industrial processes like oxidation roasting, sulfidization roasting, chloridization roasting, volatilization processes, direct reduction processes (*e.g.*, sponge iron manufacturing), high-temperature corrosion of metals in different gaseous atmospheres, chemical vapor deposition processes, and reaction sintering of ceramics.

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