**Supplementary Material**

**APPENDIX A**

**The Gibbs free energy change of a chemical reaction as a function of temperature**

1. Why*T* *A**BT* *CT* ln*T* ?

For a chemical reaction at a constant atmospheric pressure

Reactant **1** + Reactant **2** + ••• + Reactant ***i*** = Product **1** + Product **2** + ••• + Product ***j***

The term *T* defines the Gibbs free energy change in increase at temperature T if the

reaction proceeds completely. It can be calculated by

 (Equation 1)

 Products Reactants

 (Equation 2)

Where Gibbs free energy per mole for a component *i is* equal to its chemical potential *μi*, and equals to the sum of Gibbs free energy of all products *j* minus the sum of Gibbs free energy of all reactants *i*. If <0, the chemical reaction can proceed spontaneously; If =0, the chemical reaction is at equilibrium; if >0, the chemical reaction can only proceed with external energy inputs. At temperature *T*, the Gibbs free energy of a species can be expressed by its definition *G = H – TS* [84].

 (Equation 3)

Where the enthalpy term is calculated through and the entropy term is calculated through [1]. Since the specific heat *Cp* (at constant pressure) does not vary too much with respect to temperature *T* [85], it is assumed to be constant in the present work, as in case of most of the literature [86]. Equation 3 can be therefore written as

*a* *bT* *cT ln T* (Equation 4)

Where *a*, *b* and *c* are numerical coefficients. Equation 4 is also termed the Gibbs free energy of a species compared to a stable element reference state (SER) [87]. Combining Equation 1 and Equation 4, the term *T* can be finally expressed by

*T* *A**BT* *CT* ln*T* (Equation 5)

The original expression for Gibbs free energy of a species as a function of temperature (which is derived by statistical thermodynamics) [86] is given in terms of an infinite series as

*a* *bT* *cT lnT* *dT2* *eT3* *f /T* … (Equation 5)

Usually only the first two or three terms are needed, as used by many researchers to calculate

phase diagrams (in particular CALPHAD) [86, 88]. The use of first three terms is already enough to give a near perfect (suggested by R-square value) fit for the Gibbs free energy data quoted from NIST [89].

2. How to get *A*, *B* and *C*?

The first step is to obtain the Gibbs free energy values for each species using the NIST

thermochemical table [6]. Values for species at different temperatures are summarized in Table 3, 4, and 5. The second step is to calculate at each temperature *T* using Equation 1. The third step is to plot the 11 pairs of dots (*T*, ) and fit the dots to Equation 5. An example is shown in Figure 10, where the Gibbs free energy function of the reaction

4Cu + O2 2Cu2O is obtained using such method. The quality of fitting is also assessed using residual analysis.



Fig. 1 Ternary phase diagram of Al-Cu-O2 at 750⁰C showing isothermal sections