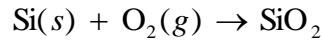


Appendix A: The Thermodynamics of Oxygen in Silicon

The formation of oxide precipitates within a silicon crystal lattice has been treated in general; however it is instructive to consider actual quantitative data. For convenience, an oxide precipitate is assumed to be a small, spherical particle of SiO₂ embedded within an otherwise perfect silicon crystal. Of course, the standard formation reaction for silicon dioxide is as follows:



As a matter of chemistry, a standard formation reaction defines a process for which one mole of some material (in this case, SiO₂) is formed from corresponding elements in standard state. (Here, this is crystalline silicon and oxygen gas.) Extensive tabulations of thermodynamic data for formation reactions have been compiled and are summarized for silicon, oxygen, and silicon dioxide in the following table:

Thermodynamic Potentials of Silicon, Oxygen, and Silicon Dioxide:

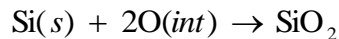
	$\Delta H_f^{\circ*}$	$\Delta G_f^{\circ*}$	$S^{\circ**}$
Si(<i>s</i>)	0	0	18.81 4.50
O ₂ (<i>g</i>)	0	0	205.152 49.03
SiO ₂ (<i>quartz</i>)	-910.7 -217.7	-856.3 -204.7	41.46 9.909
SiO ₂ (<i>cristobalite</i>) [†]	-909.5 -217.37	-855.5 -204.46	42.68 10.20
SiO ₂ (<i>tridymite</i>) [†]	-909.1 -217.27	-855.3 -204.42	43.5 10.4
SiO ₂ (<i>quartz glass</i>) [†]	-903.5 -215.94	-850.7 -203.33	46.9 11.2

* kJ/mole (italics: kcal/mole); ** J/mole°K (italics: cal/mole°K)

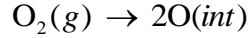
[†] data taken from Handbook of Chemistry and Physics-1st Student Ed. (1988), all other data taken from CODATA Key Values for Thermodynamics

Of course, standard conditions are defined as 298.15°K and an ambient pressure of one atmosphere. Clearly, the thermodynamic potentials for all forms of silicon dioxide (quartz, cristobalite, tridymite, and glass) are quite similar.

However, within the silicon lattice, oxygen is not in gaseous diatomic form. Therefore, to be applicable to oxide precipitation, the formation reaction must be modified as follows:

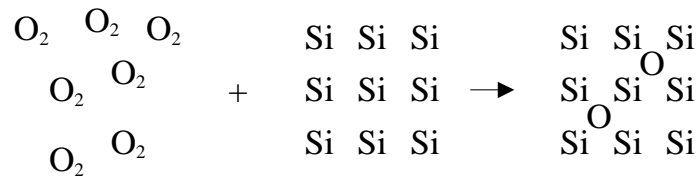


Here, $O(int)$ denotes oxygen atoms occupying interstitial sites within the silicon crystal lattice. Clearly, this reaction and the standard formation reaction are related by a third reaction that represents dissolution of oxygen gas in the silicon lattice and which can be formally written as follows:



If the standard free energy of this reaction can be found, then the standard free energy of the previous reaction is easily determined.

For this purpose, it is useful to consider the dissolution of oxygen in solid silicon as a microscopic process. Obviously, oxygen molecules must react with the silicon lattice to form oxygen interstitials. This is represented schematically below:



Of course, this is just an alternative representation of the dissolution reaction appearing above, however, the silicon lattice is included explicitly. Clearly, the overall enthalpy change for this process must include contributions from strain energy associated with an oxygen interstitial, binding energy of an oxygen molecule, and binding energy of an oxygen atom within the silicon crystal. One expects the first two of these contributions to be positive and the last one to be negative. However, with the exception of the binding energy of molecular oxygen, these contributions are not readily determined. In contrast, the entropy change can be represented as the difference of the configurational entropy change due to random distribution of oxygen atoms in interstitial sites, ΔS_O^C , and the standard entropy of oxygen gas, $S_{O_2}(T)$:

$$\Delta S = \Delta S_O^C - \frac{N_O}{2N_A} S_{O_2}(T)$$

Here, N_O is the number of oxygen interstitials and N_A is Avogadro's number. Of course, a standard entropy is also associated with the silicon lattice itself; however, if the lattice is not disrupted by oxygen interstitials, this entropy can be taken to be unchanged when oxygen interstitials are introduced into the lattice and therefore makes no contribution to ΔS . (One should note here that ΔS is defined as the entropy change associated with the formation of N_O oxygen interstitials.)

Naturally, if N is defined as the number of interstitial sites in the crystal, then the configurational entropy change is easily represented as a binomial coefficient:

$$\Delta S = k \ln \left(\frac{N!}{(N - N_O)! N_O!} \right) - \frac{N_O}{2N_A} S_{O_2}(T)$$

As is usual, one applies Stirling's approximation to obtain:

$$\Delta S = k(N \ln N - (N - N_o) \ln(N - N_o) - N_o \ln N_o) - \frac{N_o}{2N_A} S_{O_2}(T)$$

One formally adds and subtracts $N_o \ln N$ to the quantity within the parenthesis, from which it follows that:

$$\Delta S = -k \left(N_o \ln \frac{N_o}{N} + (N - N_o) \ln \left(1 - \frac{N_o}{N} \right) \right) - \frac{N_o}{2N_A} S_{O_2}(T)$$

Clearly, one expects that N will be much larger than N_o , hence the second logarithmic term can be ignored, thus:

$$\Delta S = -kN_o \ln \frac{N_o}{N} - \frac{N_o}{2N_A} S_{O_2}(T)$$

Conceptually, it is convenient to replace absolute numbers of oxygen interstitials and interstitial sites, N_o and N , by corresponding concentrations, C_o and C . Furthermore, ΔS can be recast as a molar quantity if one rescales the right hand side by the ratio, N_A/N_o . Thus, it follows that:

$$\Delta S = -kN_A \ln \frac{C_o}{C} - \frac{S_{O_2}(T)}{2}$$

Since there are five interstitial sites per diamond cubic unit cell, it follows that C is just $5/a^3$, such that a is just the lattice parameter for silicon. Therefore, one finds that C is approximately $3.123(10^{22}) \text{ cm}^{-3}$. Furthermore, kN_A is the ordinary ideal gas constant, R , which has a nominal value of $8.31441 \text{ J/mole}^\circ\text{K}$.

The standard entropy of oxygen gas at any temperature and one atmosphere pressure can be obtained from the standard entropy at 298°K by means of the integral formula:

$$S_{O_2}(T) = \int_{298}^T \frac{C_p}{T} dT + S_{O_2}(298^\circ\text{K})$$

Here, C_p is the molar heat capacity at a constant pressure of one atmosphere. If one assumes that oxygen is an ideal diatomic gas, then C_p has the value of $7R/2$, hence it follows that:

$$S_{O_2}(T) = \frac{7R}{2} (\ln T - \ln 298) + S_{O_2}(298^\circ\text{K})$$

Alternatively, $S_{O_2}(T)$ can be determined more accurately from published curve fits for the temperature dependence of constant pressure heat capacity, $C_p(T)$.

$$C_p(T) = a + bT + cT^2 + \frac{d}{T^2}$$

Here, a , b , c , and d , are empirical coefficients. Thus, one obtains:

$$S_{O_2}(T) = \int_{298}^T \left(\frac{a}{T} + b + cT + \frac{d}{T^3} \right) dT + S_{O_2}(298^\circ\text{K})$$

For convenience, an aggregate coefficient, B , can be defined in terms of a , b , c , d , and the standard entropy of oxygen gas:

$$B = a \ln 298 + 298b + (298)^2 \frac{c}{2} - \frac{d}{2(298)^2} - S_{O_2}(298^\circ\text{K})$$

Hence, $S_{O_2}(T)$ has the following form:

$$S_{O_2}(T) = a \ln T + bT + \frac{cT^2}{2} - \frac{d}{2T^2} - B$$

For oxygen gas, published values for a , b , c , and d are 34.602 J/mole $^\circ\text{K}$, 1.0795(10 $^{-3}$) J/mole $^\circ\text{K}^2$, 0 J/mole $^\circ\text{K}^3$, and -785377 J $^\circ\text{K}$ /mole, respectively. From these values, one finds B equal to -3.2777 J/mole $^\circ\text{K}$.

Obviously, it follows from the fundamental definition of Gibbs free energy that for the oxygen dissolution reaction:

$$\Delta G(T) = \Delta H(T) + RT \ln \frac{C_O}{C} + \frac{TS_{O_2}(T)}{2}$$

Obviously, ΔH is unknown. However, a method for the determination of ΔH is afforded by the oxygen solubility equilibrium. Of course, ΔG vanishes if dissolved oxygen is in equilibrium with ambient oxygen gas. Therefore, it follows that:

$$\Delta H(T) = -RT \ln \frac{C_O^{sat}(T)}{C} - \frac{TS_{O_2}(T)}{2}$$

Here, $C_O^{sat}(T)$ is saturated interstitial oxygen concentration at an absolute temperature, T . As shown in the following figure, this quantity has been determined experimentally over the temperature range 1000-1300 $^\circ\text{C}$:

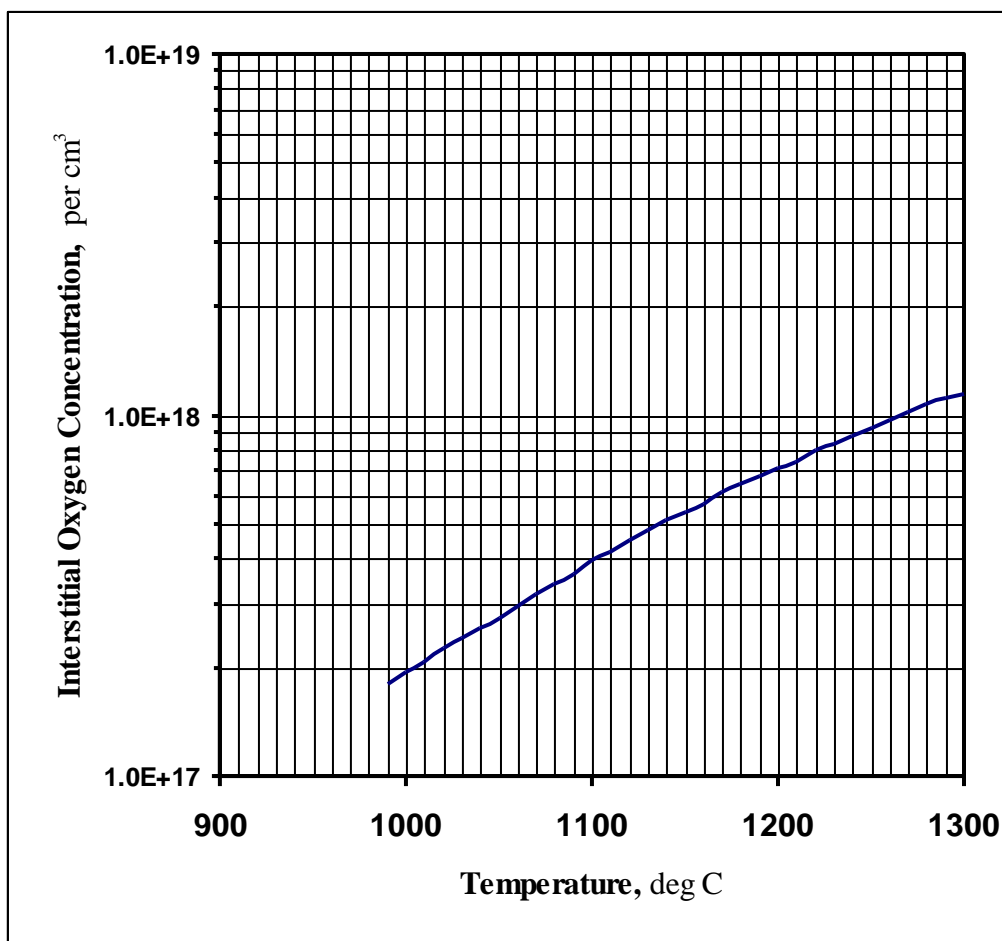


Fig. A1: Interstitial oxygen solubility as a function of temperature

Clearly, the saturated oxygen interstitial concentration varies from 10^{17} to 10^{18} cm^{-3} over the given temperature range. This is consistent with typical oxygen concentrations observed in CZ silicon wafers. Furthermore, it seems clear from the trend, that the solid solubility of oxygen in silicon should further decrease when extrapolated to lower temperatures. This effect is likely the result of an increased strain energy contribution to enthalpy due to increased lattice rigidity at lower temperatures. Accordingly, if these concentrations are used to determine $\Delta H(T)$, one finds that resulting values are negative, but relatively small. Of course, negative values imply that energy is released when oxygen dissolves in a silicon crystal. This can be rationalized if one considers experimentally measured binding energies. In particular, Si-Si and O-O binding energies are observed to be 326.8 kJ/mole (78.1 kcal/mole) and 498.34 kJ/mole (119.106 kcal/mole), respectively. These can be compared to the Si-O binding energy, which is found to be 798.7 kJ/mole (190.9 kcal/mole). Clearly, the formation of Si-O bonds from Si-Si and O-O bonds is strongly exothermic. (This is also clear just from the large, negative formation enthalpy of silicon dioxide.) However, lattice strain largely offsets this so that the magnitude of the enthalpy of formation for oxygen interstitials is fairly

small. Calculated values for the enthalpy of formation for oxygen interstitials is given in the following figure:

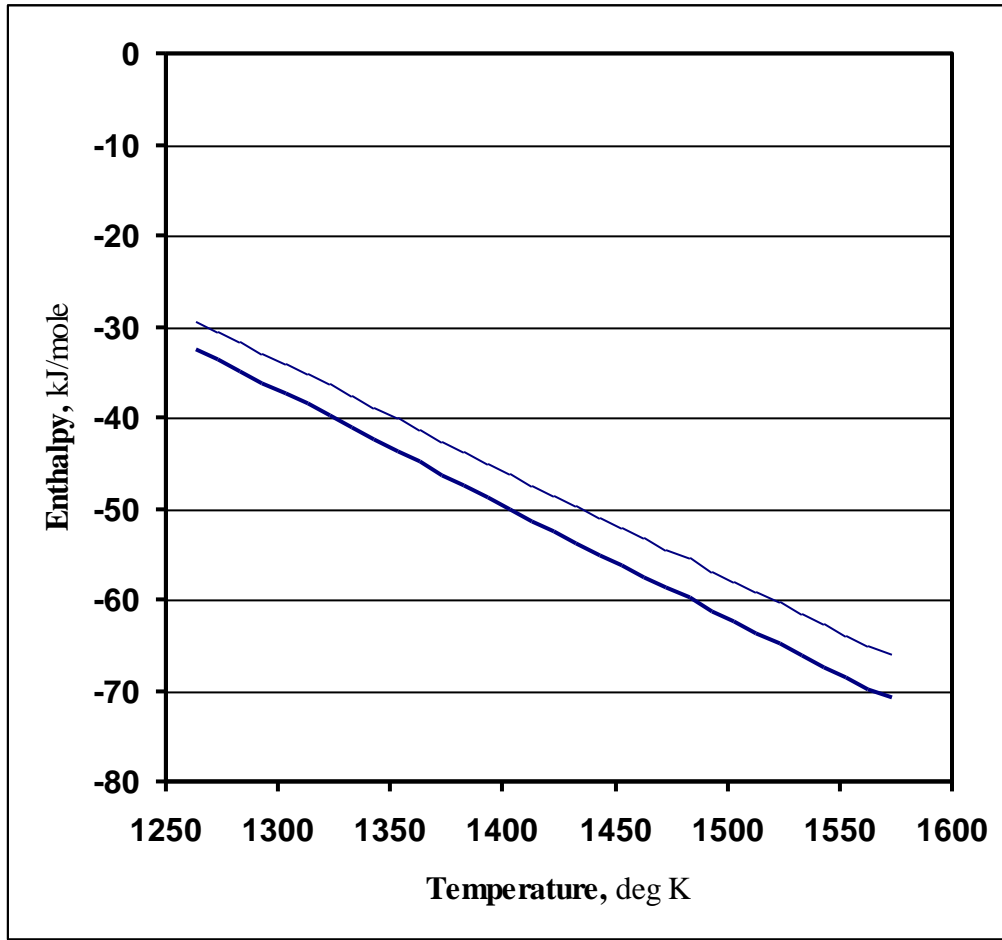


Fig. A2: Enthalpy of formation of interstitial oxygen as a function of temperature (Heavy line: C_p obtained from empirical curve fit; Light line: C_p taken as $7R/2$)

Here, C_p has been estimated both from an empirical curve fit (heavy line) or as a constant, $7R/2$ (light line). The difference is found to be only about 3 kJ/mole and a simple linear fit is quite sufficient to describe the temperature dependence of both results. Hence, $\Delta H(T)$ can be represented by the empirical linear expression:

$$\Delta H(T) = c_p T + \Delta H_0$$

From the curve fit data, the parameters, c_p and ΔH_0 are found to be -0.12459 kJ/mole $^\circ$ K and 124.87 kJ/mole, respectively. Similarly, for C_p taken as $7R/2$, c_p and ΔH_0 are found to be -0.11873 kJ/mole $^\circ$ K and 120.52 kJ/mole, respectively. This expression may be substituted into the expression for ΔG to obtain the empirical result:

$$\Delta G(T) = \Delta H_0 + T \left(c_p + R \ln \frac{C_o}{C} + \frac{S_{O_2}(T)}{2} \right)$$

This is the Gibbs free energy of formation per mole of oxygen interstitials for an elemental silicon crystal having an oxygen interstitial concentration of C_o .

Conventional enthalpy of formation of SiO_2 as a function of temperature is readily obtained by integrating over the heat capacity for SiO_2 as follows:

$$\Delta H_{f_{SiO_2}}(T) = \int_{298}^T C_p(T) dT + \Delta H_{f_{SiO_2}}(298^\circ K)$$

Again, as in the case of elemental oxygen, $C_p(T)$ for SiO_2 as is expressed as an empirical curve fit. This result is then combined with $\Delta H(T)$ for oxygen dissolution to obtain the quantity, ΔH_{SiO_2} , hence:

$$\Delta H_{SiO_2}(T) = \Delta H_{f_{SiO_2}}(T) - 2(c_p T + \Delta H_0)$$

This is represented by the figure:

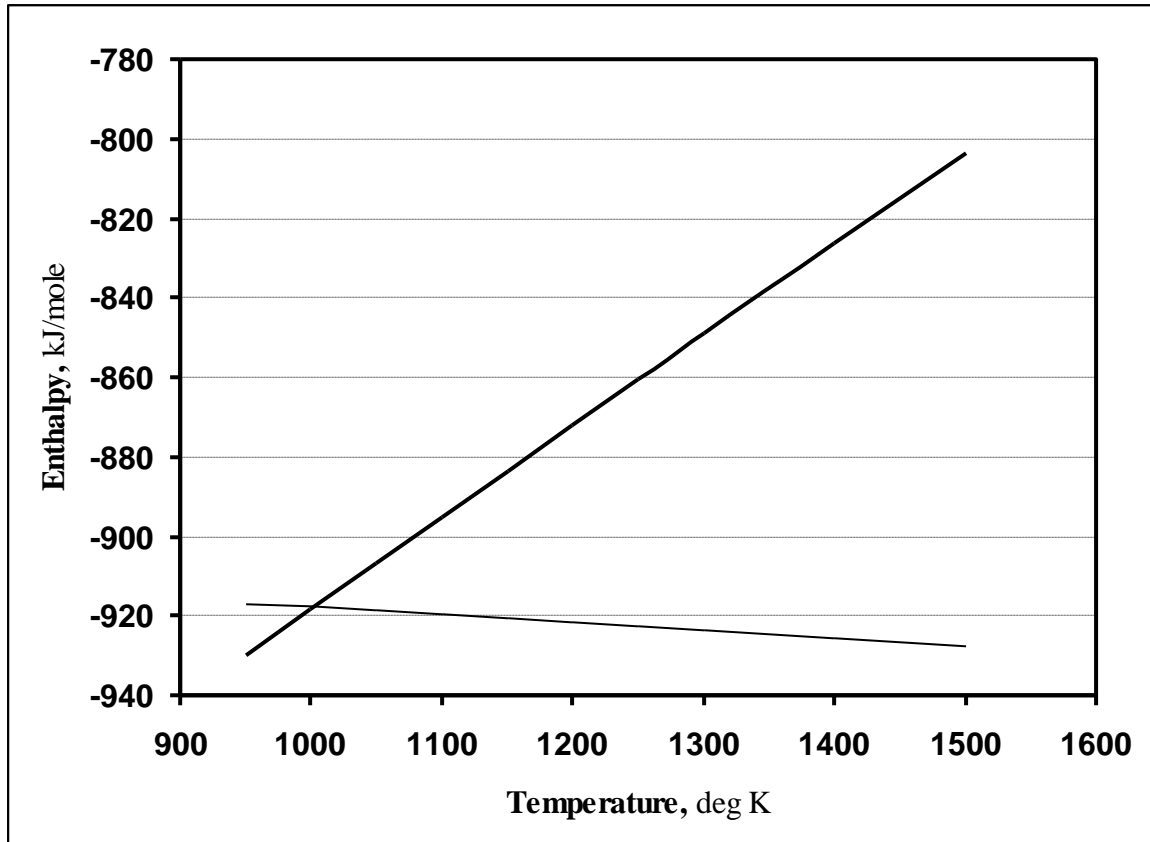


Fig. A3: Enthalpy of formation of bulk silicon dioxide in silicon as a function of temperature

Here, ΔH_{SiO_2} , defined as enthalpy of formation of bulk silicon dioxide from elemental silicon and oxygen interstitials (ignoring surface and strain energies associated with precipitates), corresponds to the heavy plot. This is contrasted with ordinary enthalpy of formation of SiO_2 (corresponding to the light plot). Clearly, over the temperature range 1000-1300°K, ΔH_{SiO_2} varies only by about 120 kJ/mole.

Of course, entropies for silicon, oxygen, and silicon dioxide can be determined as a function of temperature in an entirely analogous fashion. These quantities can be combined with the enthalpy of formation obtained previously to obtain the conventional Gibbs free energy of formation of SiO_2 as a function of temperature. Naturally, the resulting Gibbs free energy of formation is then combined with $\Delta G(T)$ for oxygen dissolution to obtain the quantity, ΔG_{SiO_2} , hence:

$$\Delta G_{\text{SiO}_2}(T) = \Delta G_{f\text{SiO}_2}(T) - 2\Delta H_0 - T \left(2c_p + 2R \ln \frac{C_{\text{O}}}{C} + S_{\text{O}_2}(T) \right)$$

As before, this relation is represented figuratively as follows:

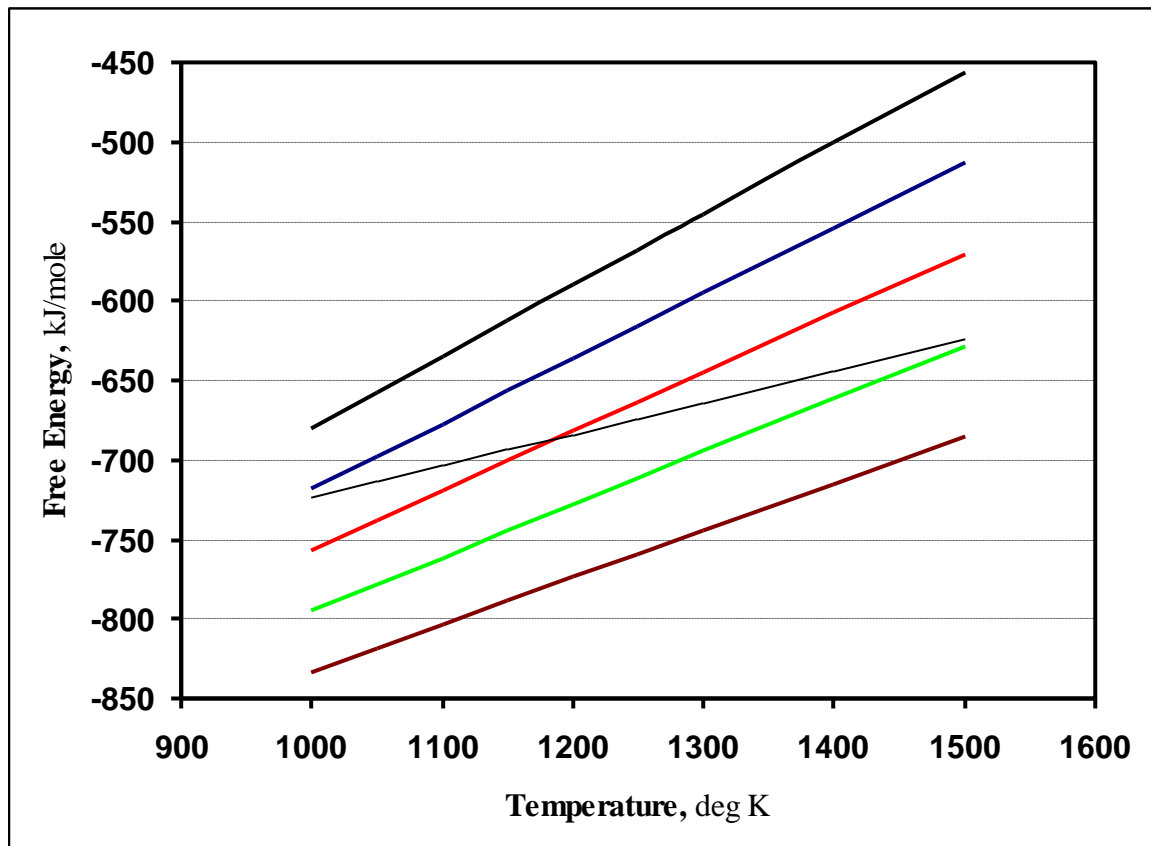


Fig. A4: Gibbs free energy of formation of bulk silicon dioxide in silicon as a function of temperature
black: $C_{\text{O}}=10^{14} \text{ cm}^{-3}$; blue: $C_{\text{O}}=10^{15} \text{ cm}^{-3}$; red: $C_{\text{O}}=10^{16} \text{ cm}^{-3}$; green: $C_{\text{O}}=10^{17} \text{ cm}^{-3}$; brown: $C_{\text{O}}=10^{18} \text{ cm}^{-3}$

Of course, ΔG_{SiO_2} is Gibbs free energy of formation of bulk silicon dioxide from elemental silicon and oxygen interstitials (again, ignoring any precipitate surface and strain energies). Clearly, the Gibbs free energy has a much larger temperature variation than enthalpy. Furthermore, unlike enthalpy, Gibbs free energy is a function of interstitial oxygen concentration. This is illustrated by the heavy plots of various colors in the preceding figure. As one would expect, when interstitial oxygen concentration decreases, ΔG_{SiO_2} becomes more positive (*i.e.*, oxide formation from interstitial oxygen is less favored.) As for enthalpy, the light plot corresponds to the conventional Gibbs free energy of formation of SiO_2 . Clearly, if at some temperature the ordinary Gibbs free energy of formation and ΔG_{SiO_2} are equal (*i.e.*, corresponding plots intersect), then the associated concentration of oxygen interstitials, C_{O} , can be identified with the solubility limit, *i.e.*, $\Delta G(T)$, as defined previously, exactly vanishes. Furthermore, since elemental oxygen gas is no longer a formal reactant for formation of bulk silicon dioxide from interstitial oxygen, all reactant and product phases can be considered condensed. Therefore, enthalpy, ΔH_{SiO_2} , is equivalent to internal energy, ΔE_{SiO_2} , and, likewise Gibbs free energy, ΔG_{SiO_2} , is equivalent to Helmholtz free energy, ΔA_{SiO_2} . Along with appropriate expressions for surface and strain energies, these quantities can be used to describe oxygen precipitation in silicon.