3.091 – Introduction to Solid State Chemistry

Lecture Notes No. 9a

BONDING AND SOLUTIONS

1. INTRODUCTION

Condensed phases, whether liquid or solid, may form solutions. Everyone is familiar with liquid solutions. These solutions are created by either mixing two miscible liquids or by dissolving a solid in a liquid solvent. Solids may, however, also form a solution. Such alloys may be metallic, ionic, or covalent. They may be crystalline or amorphous. Molecular solids may also form solutions where the interactions between molecules in the solution are secondary types of bonding such as hydrogen bonding or Vander Waals forces. .

The formation of a solution depends on the interatomic or intermolecular interactions that can take place between atoms or molecules of the pure components and also between the two different components. That is, whether a solution can form or not depends on the properties of the pure components *and* the properties of the solution.

Consider n_A moles of pure component A being mixed with n_B moles of pure component B to form a solution. This can be represented by a reaction.

$$n_A\mathrm{A} + n_B\mathrm{B} \rightleftarrows (n_A\mathrm{A}: n_B\mathrm{B})_{\mathrm{soln}}$$

Whether or not the right hand side of this equation is favored depend on both the solution product and the pure reactants. For example, the solution might be favored if A and B interact strongly. On the other hand, the solution may not form if either A or B interacts more strongly with itself. It is this simple concept that will be discussed in this chapter.

The interactions of atoms and molecules in solutions consist of two types; enthalpic and entropic. The enthalpic interaction is composed of the “bonds” that develop between nearest neighbors. (We are considering only localized bonding in condensed phases.) The sum total of the energy of all these bonds is the cohesive energy of the solution. The bonds may be metallic, ionic, or covalent. They may also be secondary bonds, as in the case of molecular crystals or liquids, such as hydrogen bonding or Vander Waals forces as mentioned above.

We will also discuss an “entropic” contribution to the interaction energy in solution. This strange factor results from the fact that solutions are *more probable* than pure substances. That is, there are the many ways solute atoms can be arranged in solution to give the same total cohesive energy. This contrasts with the pure substances A and B, which can only each be arranged one way. The enthalpic and entropic terms will be treated separately.

2. COHESIVE ENERGY OF A SOLUTION

The cohesive interactions in condensed phase, whether liquid or solid, can be approximated by the bonding that occurs between atoms or molecules and their nearest neighbors. The location and number of nearest neighbors is approximated by considering the condensed phase to be structured like a lattice with lattice sites occupied by atoms or molecules. This lattice will, of course, be the crystal structure the condensed phase is crystalline. The lattice model is also applicable to liquids where a lattice is chosen that can approximate the number of nearest neighbors and types of interactions though to exist in that liquid.

A lattice for pure substance A is shown in Figure 1. This lattice consists of n_A moles of A and is, for this example, a cubic lattice. Each atom of A has Z nearest neighbors and shares a bond between each of the nearest neighbors. The bond energy is denoted w_{AA} and represents the bond energy between two A atoms or molecules. For the purposes of this discussion, we will consider the bond energies to be negative. That is, it is the energy released when forming the bond.

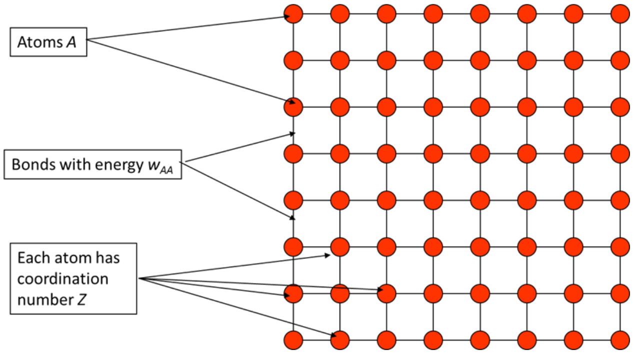

Figure 1: Lattice model for a pure A crystal.

Each lattice site is surrounded by a number of nearest neighbor sites, *Z*. That is, *Z* bonds are formed around each lattice site or *Z*/2 bonds per atom. Thus, with n_A moles of A in the lattice, the total cohesive energy of the crystal will be

$$H_A \;=\; \frac{1}{2} Z w_{AA} n_A$$

Similarly, the total cohesive energy of n_B moles of pure B on a lattice (assumed to be the same type of lattice as A) is given by

$$H_B \;=\; \frac{1}{2} Z w_{BB} n_B$$

where w_{BB} is the bond energy between two B atoms or molecules

Now let's consider the mixing of n_A moles of A and n_B moles of B. The situation is depicted in Figure 2.

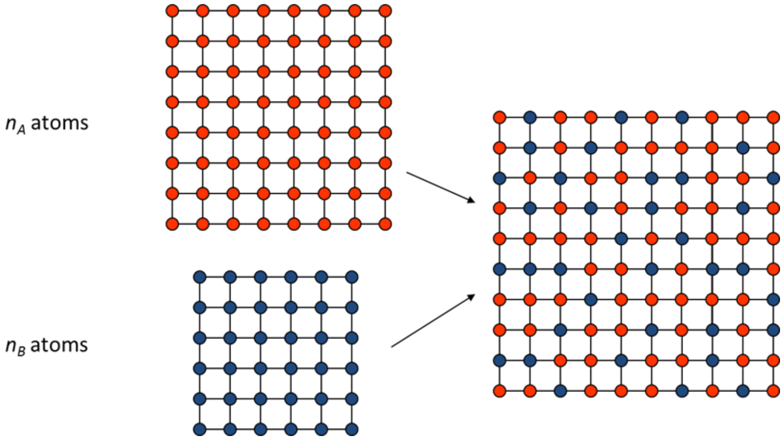

Figure 2: The mixing of n_A moles of A and n_B moles of B

Calculation of the cohesive energy of the solution is slightly more complicated. Each of the atoms (or molecules) of the solution may have nearest neighbors that are either A or B. Not only will there be homonuclear bonds between two A atoms and between two B atoms, but there will be heteronuclear interactions between A and B atoms. Thus, the cohesive energy of the solution must also include bond energies w_{AB} to represent the bonds between A and B atoms. The nearest neighbors in a solution will be composed of both A and B atoms. In a solution of n_A moles of A and n_B moles of B we have

$$\text{number of neighbor sites that are A} = \frac{n_A}{n_A + n_B} \cdot Z = x_A Z$$

$$\text{number of neighbor sites that are B} = \frac{n_B}{n_A + n_B} \cdot Z = x_B Z$$

where x_A and x_B are the mole fractions of A and B respectively. One can calculate the total cohesive energy of the solution by summing the bond energy for each type of nearest neighbor in the solution. The calculation is straight forward and can be watched in a screen cast [Cohesive Energy of a Solution]. The difference between the cohesive energy of the solution and the cohesive energy of the pure crystals is found to be

$$\Delta\overline{H}_{soln} = \frac{Z}{2} \cdot \Delta w \cdot x_A x_B$$

which is the energy change per mole of solution (n_A + n_B). Δw is given by

$$\Delta w \; = \; 2w_{AB} - w_{AA} - w_{BB}$$

Now, let's take a moment to understand the signs. A solution that has more cohesive energy than the pure crystals that it is made from will release heat when it formed. The making of a solution will be *exothermic* and the $\Delta\overline{H}_{soln}$ will be negative. If the pure crystals have more cohesive energy than the solution, then the making of a solution will require energy and will be *endothermic*. The factor that determines whether making a solution will be exothermic or endothermic is Δw, which compares the magnitude of bond energy between A and B atoms to the bond energy between two A atoms and between two B atoms. Thus, a $\Delta w < 0$ means that the formation of a solution will be exothermic and a $\Delta w > 0$ yields a formation of solution that is endothermic.

How do you estimate Δw? We can estimate the pure component bond energy from the energy required to vaporize the condensed phase. The heat of vaporization is just the energy required to take atoms (or molecules) from the condensed phase (liquid or solid). It is usually reported in energy per mole or per mass. Obviously, the interatomic or intermolecular bonds must be broken in order to vaporize the material. Thus, the heat of vaporization should be proportional to w_{AA}. In the case of a solid of A, one must break Z bonds for each atom that is vaporized. Each bond is shared between two atoms so we have to be careful about over counting. Thus, if $\overline{H}_{A,vap}$ is the molar heat of vaporization, then

$$\overline{H}_{A,vap} = \; -N_A \frac{1}{2} Z w_{AA}$$

where N_A is Avagadro's number. The negative sign is because we have defined w_{AA} as a negative quantity. The same is true for B. Thus, given the heat of vaporization of the pure materials, one can estimate w_{AA} and w_{BB}.

Estimation of w_{AB} requires a bonding model. The simplest case is when the bonds are polar covalent bonds of the type we have discussed previously. We know that the polar covalent bond energy is given by

$$w_{AB} \cong -\left(\sqrt{w_{AA}w_{BB}} + K(\Delta X)^2\right)$$

where ΔX is the difference in electronegativity and *K* is 96.3 if the energies are in kJ/mole. If we substitute this expression into the definition of Δw, one finds with some simplification

$$\Delta w = \left((-w_{AA})^{1/2} - (-w_{BB})^{1/2}\right)^2 - 2K(\Delta X)^2$$

One can see from this expression the factors that make Δw either positive or negative. The first term is a square of a difference so is positive. The second term is always negative. The first term says that larger differences in magnitude of w_{AA} and w_{BB} will favor an endothermic solution. The second term says that larger differences in electronegativity will favor an exothermic solution.

3. ENTROPY AND THE FORMATION OF A SOLUTION

You might ask why a solution will form in cases where solution formation is endothermic? These are cases where there is a net loss of cohesive energy upon forming the solution. The answer lies in the probability of forming a solution. Examination of the right hand side of Figure 2 shows a lattice model of a solution. A and B atoms are distributed randomly on the lattice. The Figure shows one such arrangement but many others are possible. Each of these arrangements have essentially the same cohesive energy or are very close to one another, if we have sufficiently large numbers of atoms. Each of the specific arrangements is called a *microstate*. The total cohesive energy corresponding to the solution is called a *macrostate*. There are a very large number of microstates corresponding to the random arrangement of A and B atoms on the lattice.

The number of microstates that correspond to this solution can be calculated by a well-known statistical formula. The number of ways to distribute n_A atoms and n_B atoms on the same lattice is given by

$$\phi = \frac{(n_A + n_B)!}{n_A!\, n_B}$$

Obviously, the factorials make this a very large number indeed if molar quantities of atoms are being considered. This may be compared to the microstates where A and B atoms are arrayed on lattices representing pure components as depicted on the left in Figure 2. There is only *one* way to distribute the atoms on the pure lattices.

The large number of ways to make a solution from pure materials can sometimes overcome the loss of cohesive energy. Consider Figure 2 again in the case where solution formation is endothermic. The left-hand side of Figure 2 has more cohesive energy (more negative) than the right. The right-hand side has less cohesive energy but many more microstates with the same, but slightly higher, energy. This higher energy state is much more degenerate than the pure states of the material. That is, the macrostate corresponding to the right-hand side of Figure 2 is more probable than the macrostate on the left.

A fundamental law of nature is that it tries to reach a compromise between adopting the lowest energy and adopting an energy state that is more probable. The probability of a given macrostate is related to its *entropy, S*. The entropy is simply related to the number of microstates by this important equation

$$S = k \ln(\phi)$$

where k is the Boltzmann constant and ϕ is the number of microstates for the macrostate.

The compromise that nature makes is based on the comparison between the enthalpy change to the change in entropy when a solution is formed. This compromise is the Gibbs energy, *G*, change, $\Delta G,$ which is $G = H - TS$. A change from one state to another is accompanied by a change in Gibbs energy ΔG which is

$$\Delta G \; = \; \Delta H - T\Delta S$$

A reaction can only proceed if the Gibbs energy change is negative. The right-hand side of the Gibbs equation contains the enthalpy change as the first term. The second term is the temperature, *T* (in Kelvin), weighted entropy change. Nature's compromise depends on temperature. The formation of a solution is favored at low temperature only when the enthalpy change is negative. An endothermic dissolution can, however, happen if the temperature is high enough as the second term will eventually overcome a positive enthalpy change.

4. LIMITED SOLUBILITY AND SOLUBILITY PARAMETER

Just how endothermic can a solution be and still spontaneously form? The answer to this depends on the balance between energy and entropy that can still achieve a ΔG that is negative. It can be shown that Δw can be no more positive than a certain value in order for A to be fully soluble in B and vice versa. This value is approximately given by the following expression

$$\frac{\Delta w}{RT} < \frac{4}{Z}$$

Assume for discussion that there are six nearest neighbors in the condensed phase (Z = 6). Thus, a complete solution can form if the dissolution is endothermic only if Δw is less than $\frac{4}{6}RT$. If it is greater than that, the dissolution of A or B is limited in one another. Note that this expression says that increasing the temperature favors dissolution. That is, even if Δw is large and positive, the criteria for complete dissolution can be met at higher temperature assuming the solid does not melt first.

We can apply our bonding ideas to get an idea of what limits solubility. The simplest bonding ideas concern cases where there is no “specific” bonding between dissimilar atoms or molecules. What this means is that there can be bonding between A and B atoms or molecules but that it is similar in type to between two A atoms or molecules and two B atoms or molecule. We call this situation a “regular solution”. In this case, we make the assumption that

$$w_{AB} \cong -\sqrt{w_{AA}w_{BB}}$$

That is, the bonding between dissimilar atoms or molecules is just the geometric mean of the bonding in the pure constituents. This estimate is similar to the case of polar covalent bonding, as described above, but lacks the specific interaction of the electrons in the bonds being shared unequally between the atoms due to electronegativity differences. Substitution of this assumption into the definition Δw results in

$$\Delta w \cong \left((-w_{AA})^{1/2} - (-w_{BB})^{1/2}\right)^2$$

This expression is often written in terms of what are called solubility parameters, δ. The solubility parameter is defined in such a way that it is proportional to $-w_{AA}$. We know $-w_{AA}$ is proportional to the heat of vaporization. In addition, the solubility parameter accounts for the number of bonds per unit volume. Thus,

$$\delta_A = \frac{\bar{H}_{A,vap}}{\bar{V}_A}$$

where $\bar{V}_A$ the molar volume. The units of δ are energy divided by volume. Energy has units of pressure times volume. Thus, δ has units of pressure. It is for this reason that δ is sometimes called the "internal pressure".

What does the solubility parameter tell us about whether two substances will dissolve in one another? If we assume, $-w_{AA} \propto \delta_A$, then

$$\Delta w \propto \left(\delta_A{}^{1/2} - \delta_B{}^{1/2}\right)^2$$

It is clear from this expression that large differences in solubility parameters create endothermic dissolution of one constituent in another. That means two substances with greatly different internal pressures (δ) will not be freely soluble in one another. This is just another way of saying that two substances with different types of bonding will not be freely soluble in one another. On the other hand, two substances with similar solubility parameters (similar bonding) will be freely soluble in one another.

Chemists often say that "like dissolves like". The discussion above defines what we mean by "like". A pure constituent that has a large internal pressure will dissolve in other materials with similarly large internal pressures but not in those that have small internal pressures. Similarly, polar molecules with large heats of vaporization will dissolve in solids or liquid of other polar molecules but not in solids or liquids that are nonpolar. The reason is that these nonpolar molecules typically have much smaller heats of vaporization.

5. SOLUBILITY OF ONE METAL IN ANOTHER

An alloy is the solution of one metal in another. Alloys are extremely important in many different technologies as they can have properties that are completely different than their elemental constituents. Whether or not two elemental metals are fully soluble in one another is understandable from the bonding concepts discussed above.

The rules that help predict whether one metal will be fully soluble in one another as a substitutional alloy[1] are sometimes referred to as the Hume-Rothery rules after William Hume-Rothery, the British materials scientist. These rules are reproduced below, but I have added the internal pressure requirement from above that was developed by Joel Hildebrand, a physical chemist.

Crystal structure criteria: *Two metallic elements can only be fully soluble in one another if each has the same crystal structure.* The same crystal structure means that each element occupies similar lattices with the same number of nearest neighbors. Substitutional positioning of one element within the crystal of another does not require a change in bonding. Thus, one may form any composition without a change in lattice.

Atomic radii criteria: *Two metallic elements will be soluble in one another if their atomic radii differ by less than approximately 15%.* This criteria recognizes that the strain energy is associated with the substitutional incorporation of one element in the crystal of another. If the atom differs greatly in size from the host atoms of the crystal, al large strain will occur and there will be an unfavorable amount of energy associated with that strain.

Valency criteria: When one metallic element is not fully soluble in another, the maximum amount that will dissolve in one will not generally be the same as in the other. *A metal will dissolve a metal of higher valency to a greater extent than one of lower valency.* Consider an alloy of metallic elements A and B that are not fully soluble in one another. If A has a higher valency than B, then B can dissolve more A than A can dissolve B. The reason for this is behavior may vary among the elements but one way to think about it is that elements that have lower valency have, by definition, fewer electrons. They are electron deficient. Thus, a metal with a lower valency will want to dissolve a higher valency metal to become less electron deficient. Copper, for example, dissolves up to 18 atomic % aluminum but aluminum dissolves only up to 3 atomic %

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[1] Recall that there two ways to form a solution on a crystal lattice. The first is *substitutional* where solute atoms ocuppy the same sites as the solvent atoms. The second is *interstitial* where the solute atoms occupy sites between the solvent atoms.

copper. Aluminum has a higher valence than copper. Another way to say that is that copper is more electron deficient than aluminum.

Electronegativity criteria: *Metals with large difference in electronegativity will tend to form compounds rather than alloys.* The formation of compounds will reduce the solubility of one metal in another. A large electronegativity difference between one element and another means that electrons will tend to be donated from one element to the other. The elements will want to form an ordered array with the differing elements sitting next to one another. This is the formation of a compound.

Internal pressure difference criteria: *Metals with large difference in internal pressure (solubility parameter) will have limited solubility in one another.* As discussed above, the similar internal pressure between two elemental metals means that the bonding is similar between the two elements. Thus, when the internal pressures are similar, it is a “like dissolves like” situation.

6. THE SOLUBILITY PRODUCT AND EQUILIBRIUM CONSTANT

Let’s consider the situation where we try and produce a solution by dissolving a solid (solute) in another solid or liquid (solvent). We add sufficient solid so that it can no longer be made to dissolve in the solid or liquid solvent. This is the point where the two phases are said to be at equilibrium.

Consider the equilibrium of solid silver sulphate, Ag_2SO_4, and its aqueous solution. The silver ion is monovalent while the sulphate ion is divalent. Thus, the solution is actually made up of Ag^+ and SO_4^{-2} in a water solvent. The ratio of the two ions is of course 2:1 silver to sulphate ion. The reaction can be written

$$\mathrm{Ag_2SO_{4(solid)}} + \mathrm{H_2O_{(pure)}} \leftrightarrows 2\mathrm{Ag^+} + \mathrm{SO_4^{-2}} + \mathrm{H_2O_{(soln)}}$$

If we make the assumption that the properties of water do not change very much upon dissolving silver sulphate, then the water that appears on both sides is the same and can be cancelled. Thus, this reaction is often written

$$\mathrm{Ag_2SO_{4(solid)}} \overset{\mathrm{H_2O}}{\longleftrightarrow} \mathrm{2Ag^+ + SO_4^{-2}}$$

The equilibrium of silver sulphate and aqueous solution establishes concentrations of silver ion and sulphate ion that do not change with time. For any given temperature, it is found that these concentrations are related to a constant called the solubility product, $\mathrm{K_{sp}}$, where

$$\mathrm{K_{sp} = [Ag^+][SO_4^{-2}]^2}$$

The terms in brackets are concentrations such as moles per liter. Converting from one concentration unit to another is a simple matter of multiplying the solubility constant by the appropriate conversion. We will see where this equation comes from in the section below, but the general form of any equilibrium is expressed by the following reaction

$$\mathrm{aA + bB \leftrightarrows cC + dD}$$

where the lower case letters correspond to the stoichiometric constants for the reaction. Once equilibrium is established, the concentrations are related to a constant at a given temperature by

$$\mathrm{K = \frac{[C]^c[D]^d}{[A]^a[B]^b}}$$

We will see below that the solubility product is an equilibrium constant where the reactant solid is in it pure form.

7. THE ORIGIN OF THE EQUILIBRIUM CONSTANT

A stated above, the only way a reaction can proceed is if the Gibbs energy change for the reaction is negative. Another way of saying this is that a reaction is stopped (we say at equilibrium) if the Gibbs energy change is zero. Equilibrium is just a condition that the reaction to the right is exactly matched with a reaction proceeding to the left. Thus, there is no net change of reactant and products at equilibrium.

Let's consider the example of the dissolution of boron into silicon. We have discussed using boron as a p-type dopant in silicon and found that the hole concentration, and therefore the conductivity, varies with the boron concentration. Boron is substitutionally placed on the silicon lattice and is not located interstitially. What you might not realize is that there is a maximum amount of boron that can be dissolved in silicon. Indeed, only a very small amount of boron can be dissolved in silicon. Elemental boron exists is a crystal structure that is rhombohedral[2] while silicon has the diamond structure that lets each silicon have four nearest neighbors. Dissolving boron in silicon requires that it adopt a tetrahedral arrangement of nearest neighbors when it only has three electrons to share. Let's dissolution of boron in silicon as

$$x_{\mathrm{B}}\mathrm{B}_{s(\mathrm{rhom})} + \; x_{\mathrm{Si}}\mathrm{Si}_{s(\mathrm{dia})} \;\rightleftarrows\; (x_{\mathrm{B}}\mathrm{B}{:}\,x_{\mathrm{Si}}\mathrm{Si})_{s(\mathrm{dia})}$$

where x_B and x_{Si} are the mole fractions of boron and silicon, respectively. The reaction product is a solution of boron in silicon and since the boron is only slightly soluble, the structure remains the diamond structure.

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[2] Elemental boron has a very interesting crystal structure. Each boron is found to have five nearest neighbors. This may seem a bit strange as that would imply that each boron has five electrons to share. Inspection of the periodic chart says, however, that it only has three. What's happening? Closer inspection of the crystal structure reveals the answer. The structure consists of groups of twelve boron atoms arranged as an icosahedron. An icosahedron is a regular polyhedron with 20 identical equilateral triangular faces, 30 edges and 12 vertices. Each vertex has five bonds along the edges of the icosahedron. The twelve boron atoms contribute a total of 36 electrons. If there is an electron shared amongst the three atoms at the corners of each face then there are 10 electrons left to bond icosahedra to one another. These are called electron deficient bonds where the electrons are spread obver more than two atoms.

Characterizing a reaction by a change in Gibbs energy means that that the reactants and products must have a Gibbs energy of their own.

$$\Delta G = x_{\mathrm{B}} G_{B(\mathrm{dia}):x_{\mathrm{B}}} + x_{\mathrm{Si}} G_{\mathrm{Si(dia)}:x_{\mathrm{Si}}} - x_{\mathrm{B}} G^{\circ}_{\mathrm{B(rhom)}} - x_{\mathrm{Si}} G^{\circ}_{\mathrm{Si(dia)}}$$

Note carefully that the Gibbs energy for the boron in solution reflects the fact that it is in a diamond lattice rather than the normal rhombohedral lattice. There will be a energy cost associated with this change because the bonding that boron undergoes in a diamond lattice is not like the silicon it replaces.

Like most energy values one has to choose a reference energy value. When we consider a bond energy, for example, we often consider the reference state to be the atoms at infinite separation as the reference state. In the case of Gibbs energy, we will have no problem calculating the change in Gibbs energy as long as we are careful to choose the same reference state for all reactants and products. It is convention to choose the reference state as the pure substances at one atmosphere pressure. But what is the Gibbs energy of a substance when it is not pure or is not at one atmosphere pressure? It turns out that one can estimate the Gibbs energy of a substance relative to the standard pure state by the following three equations

Solutions	$G_A = G^{\circ}_A + \mathrm{RT}\ln x_A$ where x_A is the mole fraction of A
Gaseous components at nonstandard pressure	$G_A = G^{\circ}_A + \mathrm{RT}\ln \frac{P_A}{1\ \mathrm{atm}}$ where P_A is the partial pressure of A
Liquids or solids at nonstandard pressure	$G_A = G^{\circ}_A + V_A(P - 1\mathrm{atm})$ where V_A is the volume of liquid or solid

A close look at the correction for solutions shows that a dilute solution of a substance has a much more negative Gibbs energy than the pure substance. This reflects the fact that the solution has more entropy.

The Gibbs energies of boron and silicon in solution using the correction above are

$$G_{\mathrm{B(dia)}:x_{\mathrm{B}}} = G^{\circ}_{\mathrm{B(dia)}} + \mathrm{RTln}x_{\mathrm{B}}$$

$$G_{\mathrm{Si(dia)}:x_{\mathrm{Si}}} = G^{\circ}_{\mathrm{Si(dia)}} + \mathrm{RTln}x_{\mathrm{Si}}$$

It is observed that the amount of boron that can be dissolved in silicon is exceedingly small. Thus, x_{Si} is near 1 which makes the logarithm term above near zero. Thus, the Gibbs energy of silicon is essentially unchanged by dissolving boron into it.

We can now substitute these expressions into the equation above for ΔG which results in

$$\Delta G = \left(x_{\mathrm{B}} G^{\circ}_{\mathrm{B(dia)}} - x_{\mathrm{B}} G^{\circ}_{\mathrm{B(rhom)}}\right) + x_{\mathrm{B}} RT \ln x_{\mathrm{B}}$$

This is the Gibbs energy change per mole of solution. It can be rewritten per mole of boron which yields

$$\Delta \bar{G} = \left(G^{\circ}_{\mathrm{B(dia)}} - G^{\circ}_{\mathrm{B(rhom)}}\right) + \mathrm{RTln}x_{\mathrm{B}}$$

The difference in Gibbs energy between the boron in a diamond lattice and boron in a rhombohedra lattice is denoted $\Delta \bar{G}^{\circ} = G^{\circ}_{\mathrm{B(dia)}} - G^{\circ}_{\mathrm{B(rhom)}}$. Thus, at equilibrium when $\Delta \bar{G} = 0$, the equation above becomes

$$\ln x_{\mathrm{B}} = -\frac{\Delta \bar{G}^{\circ}}{\mathrm{RT}}$$

If the number of lattice sites in silicon per unit volume is $\hat{\rho}_{\mathrm{Si}}$, then the moles of boron per unit volume is $c_B = x_{\mathrm{B}}(\hat{\rho}_{\mathrm{Si}}/\mathrm{N_{av}})$ where $\mathrm{N_{av}}$ is Avagadro's number. Addition of $\ln(\hat{\rho}_{\mathrm{Si}}/\mathrm{N_{av}})$ to each side of the equation above yields

$$\ln c_{\mathrm{B}} = -\frac{\Delta\bar{G}^{\circ}}{\mathrm{RT}} + \ln(\hat{\rho}_{\mathrm{Si}}/\mathrm{N}_{\mathrm{av}})$$

or

$$c_{\mathrm{B}} = \exp\left(-\frac{\Delta\bar{G}^{\circ}}{\mathrm{RT}} + \ln(\hat{\rho}_{\mathrm{Si}}/\mathrm{N}_{\mathrm{av}})\right) = \begin{matrix}\text{constant for a}\\ \text{given temperature}\end{matrix} = \mathrm{K}_{\mathrm{sp}}$$

This is just the solubility product for boron dissolving in silicon. In other words, the solubility product is related to $\Delta\bar{G}^{\circ}$. We expect $\Delta\bar{G}^{\circ}$ to vary with temperature as $\Delta\bar{G}^{\circ} = \Delta\bar{H}^{\circ} - T\Delta\bar{S}^{\circ}$. Thus,

$$x_{\mathrm{B}} = \exp\left(-\frac{\Delta\bar{G}^{\circ}}{\mathrm{RT}}\right) = \exp\left(-\frac{\Delta\bar{H}^{\circ} - T\Delta\bar{S}^{\circ}}{\mathrm{RT}}\right)$$

$$\ln(x_{\mathrm{B}}) = -\frac{\Delta\bar{H}^{\circ}}{\mathrm{RT}} + \frac{\Delta\bar{S}^{\circ}}{\mathrm{R}}$$

Shown below is the saturated boron concentration in silicon as a function of temperature. This can be re plotted as ln(c) versus 1/T as shown in the following Figure making sure to use temperature in Kelvin.

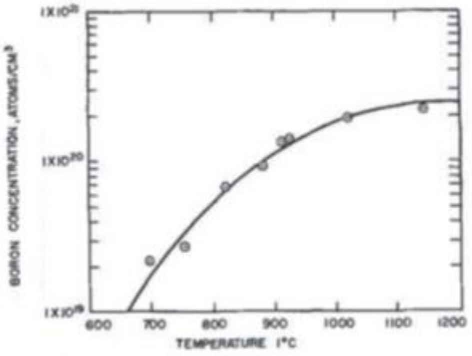

Figure 3: Saturated boron concentration in silicon as a function of temperature. G. L. Vick and K. M. Whittle, Solid Solubility and Diffusion Coefficients of Boron in Silicon, J. Electrochem. Soc. 1969, Volume 116, Issue 8, Pages 1142-1144

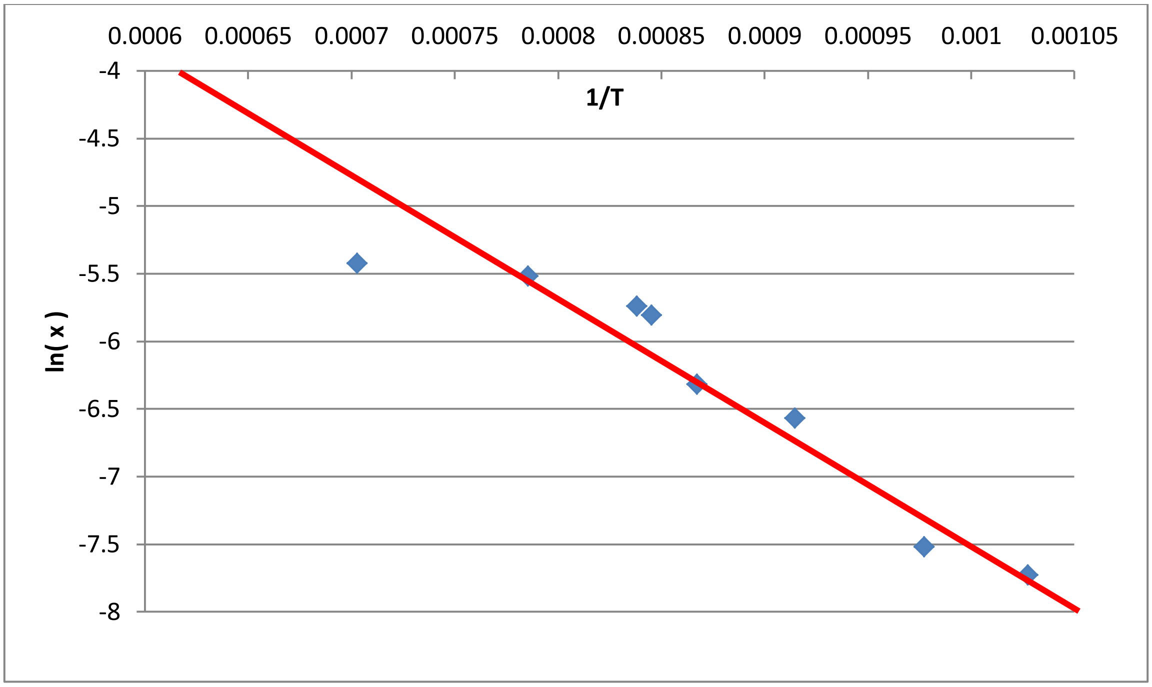

Figure 4: The natural logarithm of the saturated boron concentration in silicon (mole fraction) as a function of 1/T.

It is clear as the temperature is raised, the saturated concentration of boron in silicon increases. The behavior is roughly linear when plotted as the log of concentration versus 1/T. The slope is $-\frac{\Delta\overline{H}^{\circ}}{\mathrm{R}}$ which can be used to estimate $\Delta\overline{H}^{\circ}$. The slope in the graph above is approximately -9300 K which when multiplied by –R yields $\Delta\overline{H}^{\circ} \cong 77\ \mathrm{kJ/mole}$. You can now understand why the solubility of born in silicon is so low. Quite a large amount of energy is require to substitute a boron on a silicon site. Recall that the silicon-silicon bond energy is approximately 222 kJ/mole. Thus for every three boron atoms substituted into the silicon crystal you have to expend an amount of energy equivalent to breaking a silicon-silicon bond. A certain amount of boron does, nonetheless, dissolve in silicon despite it being so energetically unfavorable. This is the influence of entropy. There are many more ways to arrange the few boron atoms on silicon lattice that have the same energy than there is to arrange boron atoms in a pure boron crystal.