

# A Generalized Gibbs Potential Model for Materials Degradation

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## Abstract

It is well known that work done on a material by conservative forces (electrical, mechanical, chemical) will increase the Gibbs Potential of the material. The increase in Gibbs Potential can be stored in the material and is free/available to do work at some later time. However, it will be shown in this paper that while in this state of higher Gibbs potential, the material is metastable and the material will degrade spontaneously/naturally with time in an effort to reach a lower Gibbs Potential. A generalized Gibbs Potential Model is developed herein to better understand its impact on a materials degradation rate. Special attention will be given to dielectrics degradation.

## Keywords

Materials Degradation, Degradation Rate, Gibbs Potential, Gibbs Free Energy, Activation Energy, Dielectrics, Dielectric Breakdown, Time-Dependent Dielectric Breakdown, TDDDB, Bond Breakage, Thermochemical E-Model

## 1. Introduction

Evidence of materials degradation is all around us. With time, brick walls tend to crack, crumble and eventually fall. Paint on a house tends to crack and peel. Metals tend to oxidized/corrode. Our teeth tend to decay, require fillings, and may eventually require extraction. Semiconductor devices tend to degrade and eventually fail. All materials tend to degrade with time and thus, all devices built from such materials tend to eventually fail [1].

In physics and engineering, materials degradation mechanisms occur under many names: corrosion, fatigue, cracking, delamination, stress relaxation, hysteresis, charge trapping, time-dependent dielectric breakdown, surface inversion, electro-migration, stress-migration, etc. The list of degradation mechanisms is

seemingly endless and the consequences of degradation are very costly. For example, billions of dollars are spent each year in efforts to slow down just one of these degradation mechanisms: corrosion [2]. While materials degradation is usually described in macroscopic terms (such as the term corrosion), it will be shown that the root-cause of degradation generally starts at the microscopic/molecular level.

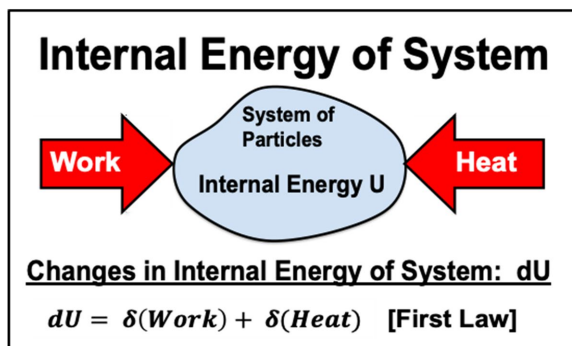
A material degradation rate (at a fixed temperature) is generally controlled by the activation energy required for the degradation process to proceed [1] [3]-[5]. The purpose of this work is to understand the underlying fundamental physics that controls this inevitable degradation process and learn how we might, at the very least, control the degradation rate. It will be shown that any external force/stress on material that increases the Gibbs Potential will serve to lower activation energy needed for the degradation process to proceed. Even a slight reduction in the activation energy can sometimes have a major impact on a materials degradation rate.

## 2. System Internal Energy

The internal energy  $U$  of a system of particles (solids, liquids, gases, plasmas) is the sum of the kinetic and potential energies of all the particles in the system. This internal energy can be increased (as described by the First Law of Thermodynamics) by doing work on the system and/or by the addition of heat to the system, as illustrated in **Figure 1**. The First Law of Thermodynamics (energy conservation) can be stated simply: [6]

$$dU = \delta(Work) + \delta(Heat). \tag{1}$$

The use of  $\delta$  on the right side of Equation (1) is a reminder that these terms are not exact differentials. They depend on the details of how the work is done and how the heat is added.



**Figure 1.** Internal energy of a system can be increased by work being done on the system and/or by heat additions to the system.

If the work done on the system is by a conservative force  $\xi$ , then the potential energy of the system will increase. Several generalized conservative forces and their differential work contributions to the system are shown in **Table 1**.

**Table 1.** Differential work done on a system by conservative forces [6].

Materials/Devices	Type of Work	Intensive and Extensive Variables	Differential Work $\delta w$ Done on Material/Device
Fluids	Mechanical	Pressure $p$ and Volume $V$	$-pdV$
Elastic Filaments	Mechanical	Force $F$ and Length $L$	$FdL$
Solids	Mechanical	Mechanical Stress $\sigma$ and Volume $V$	$\sigma dV$
Dielectrics	Electrical	Electric Field $E$ and Polarization $P$	$EdP$
Magnetics	Electrical	Magnetic Field Intensity $H$ and Magnetization $M$	$HdM$
Batteries	Electrochemical	Voltage $V$ and Charge Stored $Q$	$VdQ$
Fuel Cells	Chemical	Chemical Potential $\mu$ and Mole Number $N$	$\mu dN$

The differential work contributions to a system by conservative forces can be written as:

$$\delta(\text{Work}) = \sum_i \xi_i d\varepsilon_i = -pdV + FdL + \sigma dV + EdP + HdM + \dots \quad (2)$$

As for adding heat  $\delta Q$  to the system, it will be assumed that the heat is added in a quasi-static reversible fashion such that it can be described by the Second Law of Thermodynamics:

$$\delta(\text{Heat}) = TdS, \quad (3)$$

where  $T$  system temperature and  $dS$  is the change in system entropy [7]. Note that as we add heat to the system, then the system entropy will increase. If heat is removed from the system, then the entropy of the system decreases. The total change in internal energy of the system can now expressed by the First Law:

$$\Delta U = \delta(\text{Work}) + \delta(\text{Heat}) = \sum_i \xi_i d\varepsilon_i + T\Delta S. \quad (4)$$

### 3. Gibbs Potential/Free-Energy

The Gibbs potential  $G$  for a system of particles (plasmas, gases, liquids, or solids) is defined as:

$$G = U - TS. \quad (5)$$

The Gibbs potential is defined in such a way that any natural/spontaneous changes in the Gibbs potential  $\Delta G$  must lead to a lower Gibbs potential.  $U$  can be lowered by the natural/spontaneous bonding of electrons and protons to form atoms, bonding of atoms to form molecules, and finally the bonding of molecules to form solids. Thus, at lower temperatures, bonded molecules in a solid will have a lower Gibbs potential. However, at elevated temperatures, an increase in entropy (chaos) can lead to a lower Gibbs potential. This is why, with ever-increasing temperatures, solids turn into liquids, liquids turn into gases, and gases turn into plasmas (these are generally referred to as the four states of matter).

The change in Gibbs potential for a system (at a fixed temperature) can be written as

$$\Delta G = \Delta U - T\Delta S . \tag{6}$$

Inserting Equation (4) into Equation (6), one obtains:

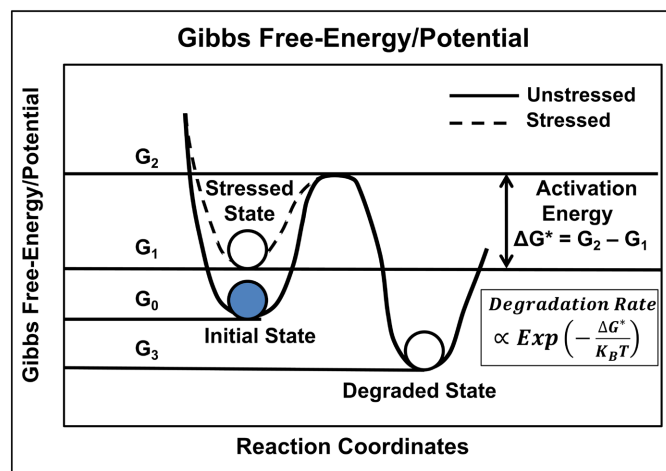
$$\Delta G = \delta(\text{Work}) = \sum_i \xi_i d\varepsilon_i . \tag{7}$$

One can see that work done on a system (by conservative forces) will increase the Gibbs potential. This increase in Gibbs potential is the amount of energy that can be stored in a system and that can be used (at some later time) to do work on the environment. Examples of energy storage devices/materials are alluded to in **Table 1**: batteries, fuel cells, pressure vessels, dielectrics, magnetics, elastic materials, etc. Because the stored energy is available to do work, it has historically been described as “free energy”. However, while in this stored-energy state (higher Gibbs Potential) the system is metastable and will look for ways of spontaneously/naturally finding lower Gibbs potential states. This is the fundamental physics behind materials degradation.

The rest of our degradation focus will be primarily be on degradation mechanisms in solids. From here on, we will refer to any solid in a state of higher Gibbs Potential (due to work done on the solid by conservative forces) as a stressed state. The stressed state will have a higher Gibbs potential and thus a lower activation energy is needed for the degradation to proceed (as illustrated in **Figure 2**). Any reduction in the activation energy will serve to accelerate the degradation rate given by:

$$\text{Degradation Rate} \propto \exp\left(-\frac{\Delta G^*}{K_B T}\right), \tag{8}$$

where  $\Delta G^*$  is the activation energy needed for the reaction to proceed and  $K_B$  is Boltzmann’s constant [8].



**Figure 2.** Any increase Gibbs Potential/Free-Energy for a solid material (stressed state) will serve to lower the needed activation energy for degradation to proceed.

## 4. General Expression for Gibbs Potential

For a conservative stress  $\xi$  acting on a system (at a fixed temperature), the change in the Gibbs Potential can be expressed as a series expansion (see Appendix A):

$$\Delta G(\xi, T) = T \sum_{m=1}^{\infty} a_m \left( \frac{\xi}{T} \right)^m. \quad (9)$$

From here out, we will refer to Equation (9) as the generalized Gibbs Potential for a stressed system. Keeping terms in the expansion only through second order (justification will be given shortly), one obtains:

$$\Delta G(\xi, T) = \Delta U - T\Delta S = \delta(\text{Work}) = a_1 \xi + \frac{a_2}{T} \xi^2. \quad (10)$$

One can see (from the above equation) that the linear and quadratic terms can have an impact on both the internal energy and the entropy. The impact of the stress  $\xi$  on system entropy is given by:

$$T\Delta S = -T \left( \frac{\partial \Delta G}{\partial T} \right)_{\xi} = \frac{a_2}{T} \xi^2, \quad (11)$$

and the impact of the stress  $\xi$  on the system internal energy is given by:

$$\Delta U = \Delta G + T\Delta S = a_1 \xi + 2 \frac{a_2}{T} \xi^2. \quad (12)$$

One should note that the quadratic term has a Curie Law ( $1/T$ ) dependence. The Curie Law will be present if the stress  $\xi$  is having a significant impact on the change in system entropy. We will now investigate how well the generalized Gibbs Potential describes several actual systems.

## 5. Generalized Gibbs Potential Applied to Several Systems of Interest

### 5.1. Rigid Solids

Let us consider the simple example of a rigid body that is lifted vertically a distance  $h$  against the force of gravity. Here, the generalized force of gravity is simply  $\xi = mg$ , where  $m$  is the mass of the object and  $g$  is the acceleration of gravity. The amount of work done  $\Delta G$  on this simple system is:

$$\Delta G = \delta(\text{Work}) = h\Delta\xi. \quad (13)$$

In this example, the Generalized Gibbs Potential coefficients are simply  $a_1 = h$  and  $a_2 = 0$ . Since there is no change in entropy for this simple system, as expected from the Generalized Gibbs Potential, then  $a_2 = 0$

### 5.2. Gas or Liquid with Molecules that Possess Permanent Electric Dipole Moments

Let us now consider the example of a gas (or liquid) of  $N$  molecules, with each molecule having a permanent electric dipole moment  $p_0$ , that is free to rotate. If

we apply an electric field  $E$  to this system (of randomly oriented dipoles), then the dipole moments will try to align with the electric field  $E$  but with thermal effects (molecular collisions) trying to counter alignment. This will impact both the internal energy and the entropy of the system. Since the net dipole moment per unit volume  $P$  is induced by  $E$ , then  $P$  can be expressed as (an approximation to the Langevin equation): [9]

$$P = \frac{Np_0^2}{3K_B T} E. \tag{14}$$

Thus, the work done by the electric field on this system is given by:

$$\Delta G = \delta(\text{Work}) = \int_0^E E dP = \frac{Np_0^2}{6K_B T} E^2. \tag{15}$$

For this system, of dipoles free to rotate, the Generalized Gibbs Potential coefficients are  $a_1 = 0$  and  $a_2 = \frac{Np_0^2}{6K_B}$ . Note also, as predicted by the Generalized Gibbs Potential, the Curie Law ( $1/T$  temperature dependence) is observed.

### 5.3. Solid Dielectrics

The work done by the electric field  $E$  on any paraelectric material can be written as:

$$\Delta G = \delta(\text{Work}) = \int_0^E E dP, \tag{16}$$

where the polarization  $P$  (net dipole moment per unit volume) is induced by  $E$  and it is given by

$$P = \epsilon_0 \chi_e(T) E. \tag{17}$$

$\chi_e(T)$  is the electric susceptibility and can be expressed by Curie's law:

$$\chi_e(T) = \frac{T_0}{T} \chi_e(T_0), \tag{18}$$

where  $T_0$  is the arbitrary temperature at which the electric susceptibility is measured.

Thus, the work done on a solid dielectric system by the electric field  $E$  is given by:

$$\Delta G = \frac{1}{2} \epsilon_0 \chi_e(T_0) \left( \frac{T_0}{T} \right) E^2. \tag{19}$$

For this solid dielectric system, the Generalized Gibbs Potential coefficients are simply  $a_1 = 0$  and  $a_2 = \frac{1}{2} \epsilon_0 T_0 \chi_e(T_0)$ . Note also, as predicted by the Generalized Gibbs Potential, the Curie Law is observed.

### 5.4. Solid Magnetics

The work done by magnetic field intensity  $H$  on a paramagnetic material is given by:

$$\Delta G = \delta(\text{Work}) = \int_0^H HdM, \quad (20)$$

where  $M$  is total magnetic moment per unit volume. Since  $M$  is induced by  $H$  and can be expressed by:

$$M = \mu_0 \chi_m \left( \frac{C}{T} \right) H, \quad (21)$$

where  $\mu_0$  is the free space permeability,  $\chi_m$  is the magnetic susceptibility, and  $C$  is the Curie constant. The work done on the magnetic material (change in the Gibbs free-energy) is given by:

$$\Delta G = \delta(\text{Work}) = \frac{1}{2} \mu_0 \chi_m \left( \frac{C}{T} \right) H^2. \quad (22)$$

Thus, for this solid magnetic system, the Generalized Gibbs Potential coefficients are simply  $a_1 = 0$  and  $a_2 = \frac{1}{2} C \mu_0 \chi_m$ . Note again, the predicted Curie Law temperature dependence is observed.

### 5.5. Solid Mechanics

For work done by a mechanical stress  $\sigma$  acting on an a solid (with elastic properties) of volume  $V$ , the change in the Gibbs Potential can be written as:

$$\Delta G = \delta(\text{Work}) = \text{Volume} \cdot \int_0^\sigma \sigma d\epsilon, \quad (23)$$

where  $\epsilon$  is the mechanical strain. In the elastic region  $\sigma = Y\epsilon$ , where  $Y$  is Young's modulus. The work done on this system is

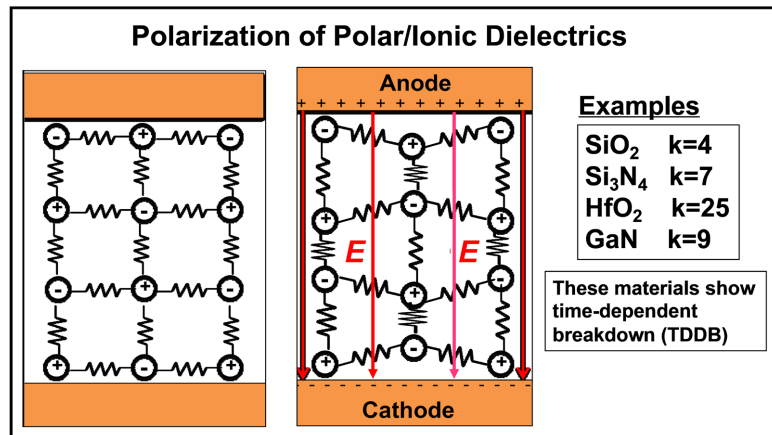
$$\Delta G = \delta(\text{Work}) = \text{Volume} \cdot \frac{1}{2} \frac{\sigma^2}{Y}. \quad (24)$$

Thus, for solid mechanics, the generalized Gibbs model coefficients are simply  $a_1 = 0$  and  $a_2 = \frac{\text{Volume}}{2Y}$ . Note in this example that the Curie Law ( $1/T$  dependence) is not present because the mechanical stress in the elastic region is having minimal impact on system entropy (atom arrangement).

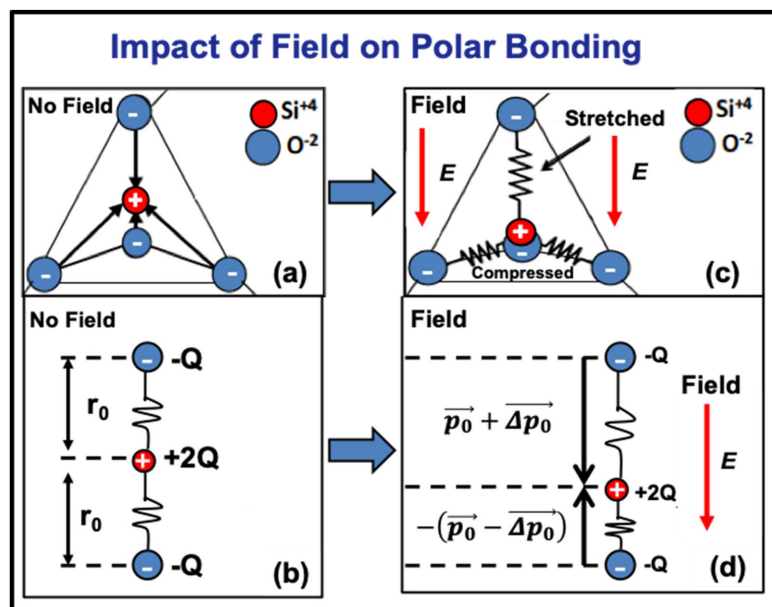
## 6. Closer Look at Generalized Gibbs Potential for Dielectric Materials

In the above examples (for elastic materials, magnetic materials, and dielectric materials), the generalized Gibbs Potential [Equation (10)] was found to be successful in predicting a quadratic term in stress  $\xi$  that would describe the amount of useful energy that could be stored in the system and is free/available to do work at some later time. The generalized Gibbs Potential was also successful in producing the Curie Law. These are significant accomplishments for the Generalized Gibbs Potential. However,  $\Delta G$  was also expected to have both linear and quadratic terms in the stress  $\xi$  variable. Does this mean that the linear term is not important for degradation? As we will now show, the answer to this question can be a strong no.

Let us reconsider the case of solid dielectric materials in more detail. **Figure 3** shows a solid dielectric material with polar/ionic bonds. When we apply a field and do conservative work on the dielectric, a polarization (net dipole moment per unit volume) is produced, but at the expense of lattice distortion. Due to the polar/ionic bonding of the molecules in the solid dielectric, we see that the polarization (due to the electric field  $E$ ) has produced alternating tensile and compressive molecular bonds within the dielectric material.



**Figure 3.** Shows a solid dielectric with significant polar/ionic molecular bonding. Under the presence of an electric field  $E$ , polarization will occur. Significant lattice distortion occurs in order to produce the net polarization. Shown are the relative dielectric constants  $k$  ( $=\epsilon_r$ ) of several polar/ionic materials.



**Figure 4.** (a) Lattice-constrained tetrahedral molecule (in  $\text{SiO}_2$ ) in the absence of field. (b) Schematic representation of dipoles with normal bonding. (c) In the presence of Field  $E$ , upper molecular bond exists in a state of tension while the lower bonds exist in state of compression. (d) Schematic representation showing the impact of field on the molecular dipole moments.

To further illustrate the impact of field on polar/ionic bonding (at the microscopic level), in **Figure 4**, we show an example of a lattice-constrained molecule with tetrahedral polar/ionic bonding that occurs in a dielectric such as SiO<sub>2</sub>.

The conservative work done by the electric field acting on the dipoles shown in **Figure 4** is given by  $\mathbf{p}_0 \cdot \mathbf{E}$ . The work done by  $E$  on the top half of the lattice-constrained tetrahedral-molecule is given by

$$w_{top} = \frac{1}{2}(p_0E + \Delta p_0E). \tag{25}$$

The work done by  $E$  on the bottom half of the molecule is given by:

$$w_{bottom} = \frac{1}{2}(-p_0E + \Delta p_0E). \tag{26}$$

The total conservative work done by the electric field on the constrained molecule becomes:

$$\delta w = w_{top} + w_{bottom} = \Delta p_0E. \tag{27}$$

Since the induced dipole moment is given by  $\Delta p_0 = \alpha E$ , then

$$\delta w = \alpha E^2, \tag{28}$$

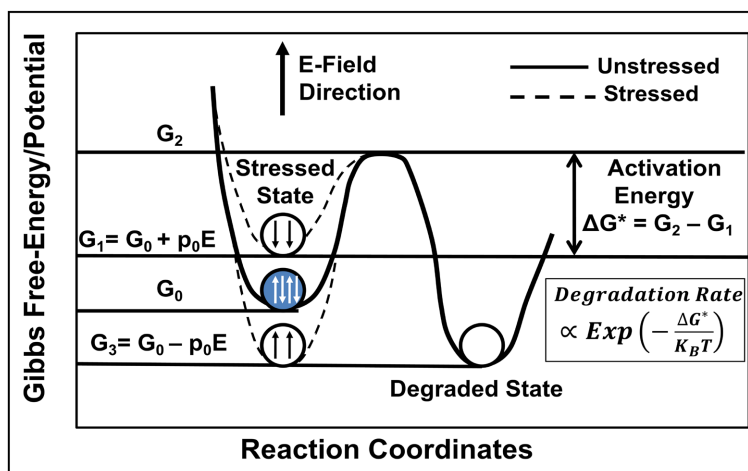
where  $\alpha$  is the molecular polarizability. The change in internal energy for the molecule becomes:

$$\Delta u = \alpha E^2 + T\Delta s. \tag{29}$$

The change in the Gibbs Potential becomes:

$$\Delta g = \Delta u - T\Delta s = \alpha E^2. \tag{30}$$

As expected, from Equation (19) for dielectrics, we find that the macroscopic useful/free-energy stored in the lattice-constrained molecule depends quadratically on the field. However, as illustrated in **Figure 5**, the degradation rate will be impacted strongly by the microscopic linear field term  $p_0E$ .

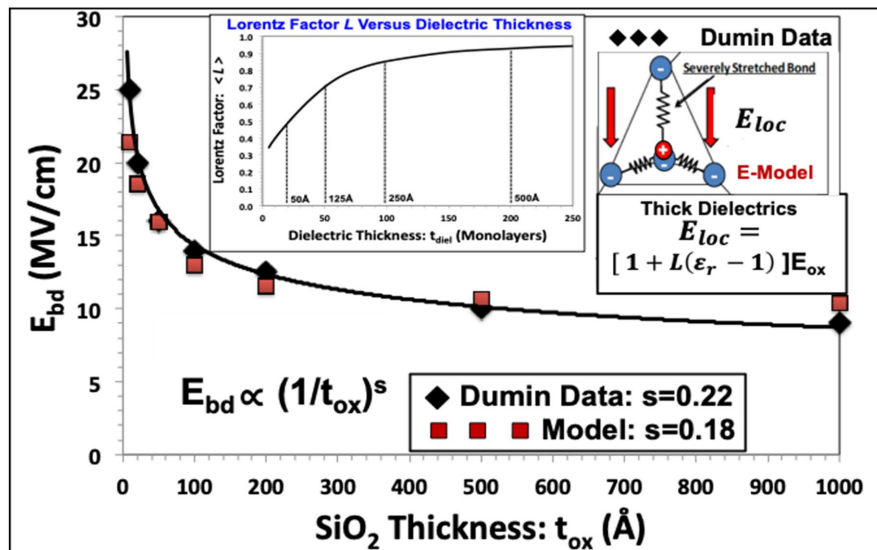


**Figure 5.** Gibbs Potential for dipoles (constrained by the lattice) to be oriented either parallel or anti-parallel to the external electric field.  $p_0$  is the dipole moment for the molecule that interacts with the field  $E$ .

One can see in **Figure 5** that we have two distinctly different potential energy states for the dipoles. Lattice constrained dipoles oriented antiparallel to the electric field will have a significantly higher Gibbs Potential and will therefore be much more unstable and more prone to bond breakage. The change in the Gibbs potential for the antiparallel portion of the molecule is given by

$$\Delta g_{\text{antiparallel}} = \Delta u - T\Delta s = \frac{1}{2}(p_0 E + \alpha E^2). \quad (31)$$

This is consistent with the Generalized Gibbs Potential Model [Equation (10)] in that it predicts both a linear and quadratic term will be present for polar/ionic dielectrics. Previously, it has been shown that the linear term ( $p_0 E$ ) is at least two orders of greater larger than the quadratic term ( $\alpha E^2$ ). [10] This means that the linear term in field  $E$  will dominate the degradation rate for polar/ionic dielectrics even though the stored free/useful energy in the dielectric is proportional to  $E^2$ . Note that the antiparallel dipoles have a higher Gibbs potential by  $+2p_0 E$  than the parallel dipoles. This makes the antiparallel dipoles much more unstable and much more prone to degradation/bond-breakage. All of this is of fundamental importance for describing time-dependent dielectric breakdown (TDDB) and is the microscopic physical basis for the thermochemical E-model. [10]



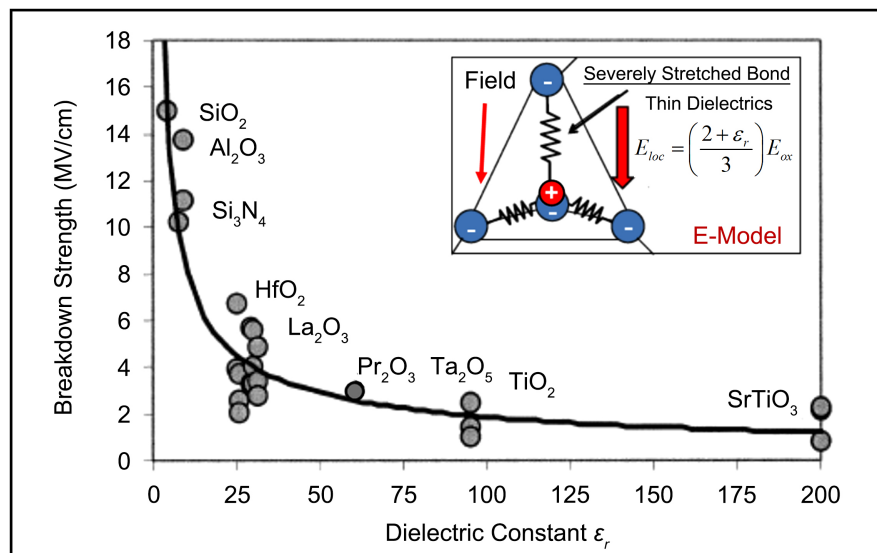
**Figure 6.** Due to the increase in the Lorentz factor with thickness, the breakdown strength of thin dielectrics tends to reduce with thickness. The insert shows the increase in Lorentz factor  $L$  with thickness. [12] The Dumin data (for 40 years of oxide thickness scaling) [13] and the model [14] are also shown.

We must also discuss the role of the local electric field. The local electric field is the field that actually distorts the polar/ionic molecules. The local electric field is the sum of the external electric field  $E$  plus the dipolar field from neighboring molecules. The local electric field is described by the Lorentz relation:

$$E_{loc} = E + L\chi_e E = [1 + L(\epsilon_r - 1)] E, \quad (32)$$

where  $L$  is the Lorentz factor,  $\chi_e$  is the electric susceptibility, and  $\epsilon_r$  is the relative dielectric constant. [11]  $L=1/3$  is normally used for very thin dielectrics but it has been shown more recently that  $L$  actually increases from  $1/3$  to asymptotically approaching 1 for thick dielectrics. [12] As shown in **Figure 6**, the increase in  $E_{loc}$  (with dielectric thickness) tends to explain the reason that thicker dielectrics have lower breakdown strength. [13] [14]

Also, as described by Equation (32),  $E_{loc}$  increases with the relative dielectric constant ( $\epsilon_r$ ) and this tends to explain why high dielectric constant materials have lower breakdown strength as shown in **Figure 7**. [15]

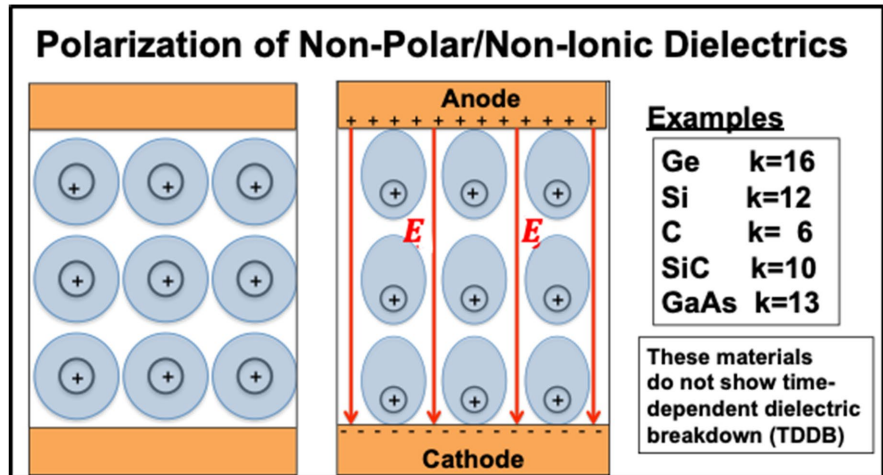


**Figure 7.** The breakdown strength of thin polar/ionic dielectrics tends to decrease with relative dielectric constant  $\epsilon_r$ .

In summary, for polar/ionic dielectric degradation, we have shown that both the linear and the quadratic terms in the Generalized Gibbs Potential Model can be important for degradation. The linear term tends to appear at the microscopic level whereas the quadratic term tends to appear at the macroscopic level. As for degradation in polar dielectrics, the linear term can be orders of magnitude greater than the quadratic term. [10]

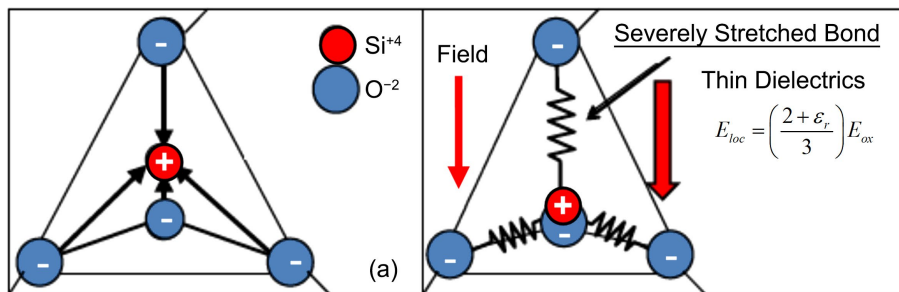
Before leaving this section, it is instructive to look at non-polar/non-ionic dielectrics. Such a non-polar solid dielectric is shown in **Figure 8**. As is illustrated, the electric-field  $E$  induces a polarization simply by the shifting of the electronic cloud(s) about each atom, thus little/no lattice distortion occurs.

Since there is little/no lattice energy going into increasing Gibbs Potential (for non-polar/non-ionic materials), then the usually dominant linear  $a_1\xi$  term in  $\Delta G$  for polar/ionic dielectrics is not relevant for non-polar/non-ionic dielectrics. This means that only the much weaker second-order quadratic  $\frac{a_2}{T}\xi^2$  term will be present in  $\Delta G$ . Thus, non-polar/non-ionic dielectrics are much more stable and much less prone to TDDB. This is shown in **Table 2**.



**Figure 8.** Shows a solid dielectric with little to no polar/ionic molecular bonding. Under the presence of an electric field  $E$ , polarization will occur due solely to the shifting of the electron cloud(s) around each atom nucleus. Shown are the relative dielectric constants  $k$  ( $=\epsilon_r$ ) of several non-polar/non-ionic materials.

**Table 2.** Impact of polar/ionic bonding on TDDB.



Material	Band Gap	Relative Dielectric Constant: $\epsilon_r$	Refractive Index Squared (@650 nm WL)	Bonding	TDDB
Diamond: C	5.4 eV	6	6	Covalent	No
Germanium: Ge	0.7 eV	16	16	Covalent	No
Silicon: Si	1.1 eV	12	12	Covalent	No
Gallium Arsenide: GaAs	1.4 eV	13	13	Covalent	No
Silicon Carbide: SiC	3.2 eV	9	7	~Covalent	No
Gallium Nitride: GaN	3.4 eV	9	5.7	~Polar	Yes
Silicon Dioxide: SiO <sub>2</sub>	8.9 eV	4	2.2	Polar	Yes
Silicon Nitride: Si <sub>3</sub> N <sub>4</sub>	5.0 eV	8	4	Polar	Yes
Tantalum Pentoxide: Ta <sub>2</sub> O <sub>5</sub>	4.4 eV	22	4.4	Polar	Yes
Hafnium Dioxide: HfO <sub>2</sub>	5.8 eV	25	3.9	Polar	Yes

Whether a dielectric is polar or non-polar can be easily identified by comparing the relative dielectric constant  $\epsilon_r$  with the refractive index  $n^2$ . If they are equal, then the material is non-polar. As for the role of leakage current through the dielectric (at elevated electric fields) possibly impacting TDDB, [16] current flow might be expected to help catalyzing the bond-breakage process and thus impacting TDDB [17], but it cannot be the fundamental mechanism for TDDB. Current flow will occur in both polar and non-polar materials, but only polar materials experience TDDB. The same can be said to be true for hydrogen release TDDB models. [18] Hydrogen release (due to current flow) might be expected for both polar and non-polar materials, but only polar materials experience TDDB.

### 7. Impact of the Generalized Gibbs Potential on Degradation Rate

A generalized Gibbs potential model for degradation in solid materials is shown in Figure 9. When a system is stressed, it forces the system into a state of higher Gibbs potential, making the system metastable and more prone to degradation. Using reaction rate theory, the rate of degradation will depend on the forward reaction activation energy  $\Delta G_0^*$  and the reverse reaction activation energy  $\Delta G_1^*$ . One can see that the forward reaction rate (degradation rate) will be strongly impacted by activation energy lowering by  $\Delta G(\xi, T)$ .

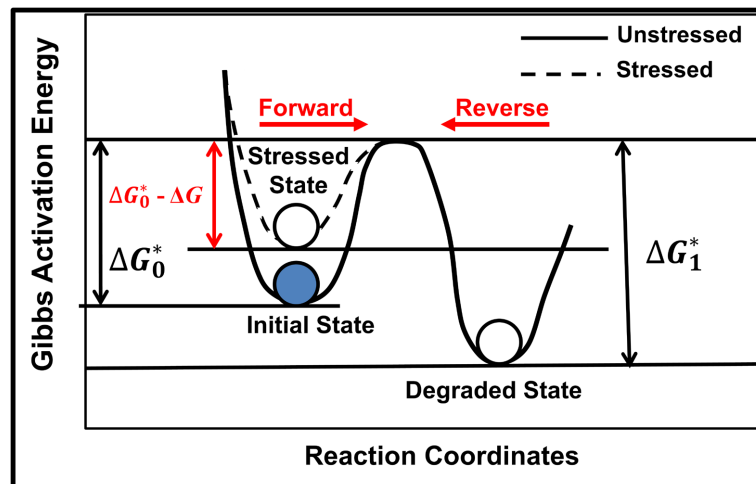


Figure 9. Driving force for degradation is reaching a lower Gibbs potential. The degradation rate is determined by the forward and reverse reaction rates. The reaction rates are controlled activation energies  $\Delta G^*$ . The impact of the stress is represented by  $\Delta G(\xi, T)$ .

From Figure 9, one can construct a net degradation rate:

$$R_{degradation} = R_{forward} - R_{reverse} = \nu_0 \left[ \exp\left(-\frac{\Delta G_0^* - \Delta G(\xi, T)}{K_B T}\right) - \exp\left(-\frac{\Delta G_1^*}{K_B T}\right) \right], \tag{33}$$

where  $\nu_0$  is the interaction/collision frequency with the potential barriers. If

$\Delta G_0^* \ll \Delta G_1^*$ , then it is rather obvious that the forward reaction dominates and the degradation rate is given simply by:

$$R_{degradation} \cong \nu_0 \exp\left(-\frac{\Delta G_0^* - \Delta G(\xi, T)}{K_B T}\right). \quad (34)$$

However, in Appendix B we discuss perhaps a more interesting case of  $\Delta G_0^* \cong \Delta G_1^*$ . In this case, the reverse reaction can be significant. For small values of stress [small values of  $\Delta G(\xi, T)$ ], Equation (33) reduces to:

$$R_{degradation} \cong \nu_0 \frac{\Delta G(\xi, T)}{K_B T} \exp\left(-\frac{Q}{K_B T}\right). \quad (35)$$

where  $Q$  is the average activation energy for the forward and reverse reactions. For large values of stress [ $\Delta G(\xi, T)$  is on the same order of magnitude as  $Q$ ], then Equation (33) reduces to:

$$R_{degradation} \cong \nu_0 \exp\left(-\frac{Q - \Delta G(\xi, T)}{K_B T}\right). \quad (36)$$

For intermediate values of stress, a simple power law is a reasonable approximation to bridge the gap between low stress [Equation (35)] and high stress [Equation (36)] conditions:

$$R_{degradation} \cong \nu_0 \left(\frac{\Delta G(\xi, T)}{K_B T}\right)^m \exp\left(-\frac{Q}{K_B T}\right). \quad (37)$$

Because the activation energy  $Q$  is usually on the order of an eV, the exponential temperature dependence tends to dominate the smaller temperature dependence in the pre-factor. For this reason, the temperature dependence in the pre-factor is often ignored or simply incorporated into  $Q$  as an effective activation energy  $Q_{eff}$ . In practice (reliability engineering), a simplified expression is typically used for degradation analysis:

$$R_{degradation} \cong B_0 \xi^n \exp\left(-\frac{Q_{eff}}{K_B T}\right). \quad (38)$$

Time-To-Failure TF models are easily determined since,

$$TF \propto \frac{1}{R_{degradation}} = A_0 \xi^{-n} \exp\left(\frac{Q_{eff}}{K_B T}\right). \quad (39)$$

## 8. Discussion

Historically, the Gibbs potential has been very important for science and engineering. As we have seen, if one does reversible work on a system against conservative forces, then Gibbs potential/free-energy will rise (potential energy is stored in system). In this case,  $\Delta G$  represents the maximum amount of useful energy that is available/free to do work at some later time. Thus, the Gibbs potential is rather ideal for describing useable energy storage. This has been the focus for the Gibbs potential since Gibbs first introduced it for chemical/fluid systems.

However, what has received much less attention is the fact that the materials, in a Gibbs potential/free-energy storage device, are metastable and the materials will degrade with time. The materials degradation not only impacts the amount of available/free-energy in the storage device but, perhaps more importantly for reliability, the degradation of the material causes eventual storage-device failure. This is seemingly a fundamental law of nature and degradation physics—*all materials/systems put into a state of higher Gibbs potential are metastable and will spontaneously/naturally degrade with time.*

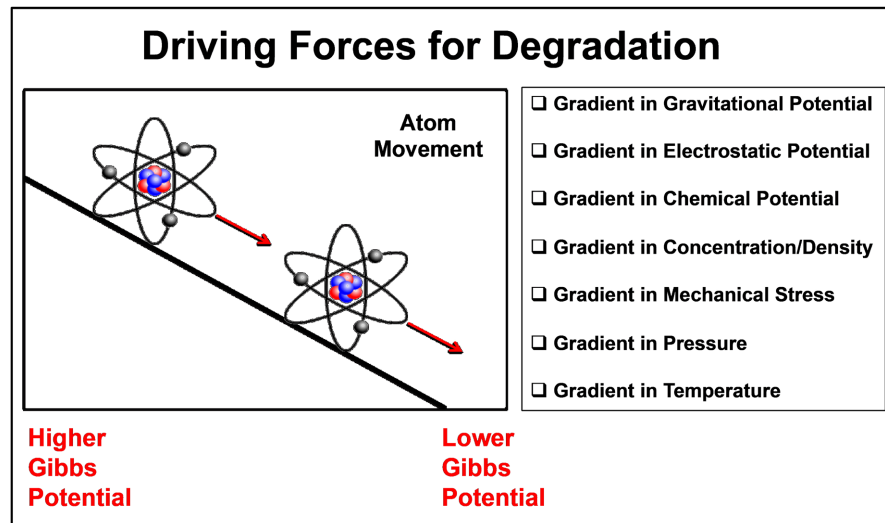
A generalized Gibbs Potential Model has been introduced here and it seems to be well suited for describing the degradation physics for materials under stress. At the most fundamental level of understanding, the Gibbs potential/free-energy has two competing terms: a *cohesive term* (where bonding is preferred) and a *dispersive term* (where bonding disruption is preferred). At lower temperatures, the cohesive term dominates. At higher temperatures, the dispersive term dominates. When we apply a generalized stress  $\xi$  to a material, it tilts the Gibbs potential/free-energy in a direction that favors the dispersive/disruptive term. We have presented a general approach to degradation physics that describes how the Gibbs potential/free-energy changes when a material is put under stress. The stress tends to lower the activation energy needed for an enhanced degradation rate.

Materials are often fabricated into metastable states that will inevitably degrade. For example, pure metals (used for their conductive properties) must be purified and fabricated for use. However, pure metals (with perhaps gold being only the exception) are not found in nature. Metals are only found in their metal-oxide state. This is because the metal-oxide state has a lower free energy than pure metal. Thus, a device fabricated with pure metal is likely to degrade by oxidation/corrosion. Important semiconductor materials such as Ge, Si, GaAs, GaN, and SiC do not exist in nature and thus must be purified and fabricated. Pure dielectrics such as SiO<sub>2</sub> are not found in nature in a purified state. Thus, materials purification and fabrication are required. All semiconductor devices (which are so important for everyday life) are fabricated from metastable materials (semiconductors, metals, dielectrics). Fabrication of these materials into metastable states has thus put them in a state of higher Gibbs potential/free-energy and they will degrade. Thus, this inevitable degradation process must be controlled through design and process.

Perhaps without realizing it, we have been using Gibbs potential all along but possibly under a different name. The historical story of Newton seeing an apple falling from a tree limb to earth is a good example. Newton described the falling-apple event as due to the force of gravity (a gradient existed in the gravitational potential). Another way of looking at this event—the apple existed in a metastable state (higher gravitational potential energy) while hanging on the tree limb. While in this state of higher Gibbs potential, microscopic/molecular degradation occurred within the apple's stem. The degradation within the stem continued until the stem could no longer support the weight of the apple and it fell. This would be a Gibbs potential explanation for the apple spontaneously/naturally falling from

the tree.

Several of the driving forces commonly used for degradation analysis are illustrated in **Figure 10**.



**Figure 10.** Several driving forces for degradation (gradients in potentials). Each driving force leads to a lower Gibbs Potential.

The historical focus of the Gibbs potential has been primarily concerned with how much recoverable energy is possible whenever a system is stored in a state of higher Gibbs potential (electrical, mechanical, chemical, etc.). While the amount of free/available energy is certainly important (from a practical engineering point of view), but perhaps something even more profound (from a reliability physics point of view) was not emphasized enough—*any system put into a state of higher Gibbs potential is fundamentally more unstable and will degrade with time*. This is apparently an important fundamental property of nature and is the driving force for degradation physics.

## 9. Summary

For a conservative stress  $\xi$  acting on a material (at a fixed temperature  $T$ ), the change in the Gibbs Potential can be expressed as a series expansion of  $\xi$  and  $T$ . Keeping terms in the expansion only through second order, it was shown that the quadratic term tends to describe the amount of useful energy (Gibbs free energy) that can be stored in a material. In addition, it was shown that the empirical Curie Law is theoretically produce. While the quadratic term predicts the amount of useful energy that can be stored in a material (a macroscopic effect), the linear term (a microscopic effect) can often dominate the degradation rate for the material while in this state of higher Gibbs potential. It was shown that, for thermally activated degradation mechanisms, the degradation rate can be described well by either an exponential or a power-law dependence on the stress  $\xi$ . This theoretical work tends to give a fundamental physics basis for the exponential and power-

law time-to-failure models that are commonly used today in reliability engineering.

## 10. Conclusion

Materials degradation is a fundamental property of nature. The degradation rate for a material (at a fixed temperature) tends to increase with the applied stress level (electrical, mechanical, or chemical). Using a Generalize Gibbs Potential, and reaction rate theory, it was shown that the degradation rate is expected to be thermally activated and linearly dependent on the stress level (for low values of stress) but exponentially dependent on the stress (for high values of stress). A power-law stress dependence and an effective activation energy is generally used for intermediate levels of stress.

## Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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## Appendix A: Generalized Gibbs Potential Model for Degradation

For a single conservative stress  $\xi$  acting on a system that produces a system response  $\varepsilon$ , the change in internal energy  $U$  can be written:

$$dU = \delta(\text{Work}) + \delta(\text{Heat}) = \xi d\varepsilon + TdS \quad (\text{A1})$$

where  $T$  is the temperature and  $dS$  is the change in entropy. Since  $U$  is a function of the extensive variables  $(\varepsilon, S)$ , one can write:

$$dU = \left(\frac{\partial U}{\partial \varepsilon}\right)_S d\varepsilon + \left(\frac{\partial U}{\partial S}\right)_\varepsilon dS. \quad (\text{A2})$$

Comparing Equations (A.1) and (A.2), one obtains:

$$\xi = \left(\frac{\partial U}{\partial \varepsilon}\right)_S \quad (\text{A3})$$

and

$$T = \left(\frac{\partial U}{\partial S}\right)_\varepsilon \quad (\text{A4})$$

Using the Euler theorem, one can write:

$$U = \left(\frac{\partial U}{\partial \varepsilon}\right)_S \varepsilon + \left(\frac{\partial U}{\partial S}\right)_\varepsilon S. \quad (\text{A5})$$

Finally, using Equations (A.3) through (A.5), we obtain:

$$U = \xi\varepsilon + TS. \quad (\text{A6})$$

The Gibbs potential/free-energy for a system (where no pdV work is being done) is defined as:

$$G = U - TS. \quad (\text{A7})$$

For the unstressed system, one has:

$$G_0 = U_0 - TS_0. \quad (\text{A8})$$

For the stressed system, one has

$$G_{stressed} = U_0 + \xi\varepsilon - TS_{stressed}. \quad (\text{A9})$$

Therefore,  $\Delta G$  becomes:

$$\Delta G = G_{stressed} - G_0 = \xi\varepsilon - T(S_{stressed} - S_0). \quad (\text{A10})$$

The Gibbs potential is a function of intensive parameters  $\xi$  and  $T$ . We will attempt to use the method of separation of variables and write Equation (A.10) as:

$$\Delta G = \xi\varepsilon - T(S_{stressed} - S_0) = f(\xi)g(T). \quad (\text{A11})$$

From Equation (A.10), we have the relations:

$$\varepsilon = \left(\frac{\partial(\Delta G)}{\partial \xi}\right)_T \quad (\text{A12})$$

and

$$(S_{stressed} - S_0) = - \left( \frac{\partial(\Delta G)}{\partial T} \right)_{\xi} \tag{A13}$$

Substituting Equations (A.12) and (A.13) into Equation (A.11), we obtain:

$$\xi g \frac{df}{d\xi} + Tf \frac{dg}{dT} = fg \tag{A14}$$

Dividing both sides of Equation (A.14) by  $fg$ , we obtain a separation of variables equation:

$$\frac{\xi}{f} \frac{df}{d\xi} + \left( \frac{T}{g} \frac{dg}{dT} - 1 \right) = 0 \tag{A15}$$

Since the independent variables are now separated, then the only way the two terms can add to zero is by both equaling some constant  $m$ :

$$\frac{\xi}{f} \frac{df}{d\xi} = m \tag{A16}$$

and

$$\frac{T}{g} \frac{dg}{dT} - 1 = -m \tag{A17}$$

The solution to Equation (A.16) is:

$$f = \xi^m \tag{A18}$$

and the solution to Equation (A.17) is:

$$g = T^{1-m} \tag{A19}$$

The full separation of variables solution becomes:

$$\Delta G = T \sum_{m=0}^{\infty} a_m \left( \frac{\xi}{T} \right)^m \tag{A20}$$

Since  $\Delta G = 0$  at  $\xi = 0$ , then the separation of variables solution reduces to:

$$\Delta G = T \sum_{m=1}^{\infty} a_m \left( \frac{\xi}{T} \right)^m \tag{A21}$$

Finally, for a stressed system we have the series expansion:

$$G_{stressed} = G_0 + T \sum_{m=1}^{\infty} a_m \left( \frac{\xi}{T} \right)^m \tag{A22}$$

### Appendix B: Net Degradation Rate for Reversible Reactions

The net degradation rate in **Figure 9** is governed by the forward and reverse reaction rates:

$$\begin{aligned} R_{degradation} &= R_{forward} - R_{reverse} \\ &= \nu_0 \left[ \exp \left( - \frac{\Delta G_0^* - \Delta G(\xi, T)}{K_B T} \right) - \exp \left( - \frac{\Delta G_1^*}{K_B T} \right) \right], \end{aligned} \tag{B1}$$

where  $\nu_0$  = the fundamental vibrational/interactional-frequency for the atoms

in the solid system and where  $\Delta G_0^*$  and  $\Delta G_1^*$  are the activation energies illustrated in **Figure 9**. We note that if  $\Delta G_0^* \ll \Delta G_1^*$ , then the forward reaction dominates and the degradation rate is given simply as:

$$R_{degradation} \cong \nu_0 \exp\left(-\frac{\Delta G_0^* - \Delta G(\xi, T)}{K_B T}\right). \quad (B2)$$

Now, let us consider the case where  $\Delta G_1^* \cong \Delta G_0^*$ . Under these conditions, the reverse reaction  $R_{reverse}$  can be significant. Rearranging Equation (B1), we obtain:

$$R_{degradation} = \nu_0 \exp\left(-\frac{\Delta G_0^* - \Delta G(\xi, T)}{K_B T}\right) \left[1 - \exp\left(-\frac{\Delta G_1^* - \Delta G_0^* + \Delta G(\xi, T)}{K_B T}\right)\right]. \quad (B3)$$

Using the identity:

$$2 \exp\left(-\frac{x}{2}\right) \sinh\left(\frac{x}{2}\right) = 1 - \exp(-x), \quad (B4)$$

One can write:

$$R_{degradation} = 2\nu_0 \exp\left(-\frac{\Delta G_1^* + \Delta G_0^* - \Delta G(\xi, T)}{2K_B T}\right) \sinh\left(\frac{\Delta G_1^* - \Delta G_0^* + \Delta G(\xi, T)}{2K_B T}\right). \quad (B5)$$

Since we are assuming that strong reverse reactions can occur only when  $\Delta G_1^* \cong \Delta G_0^*$ , then we can define an average activation energy for degradation as  $Q$ , where:

$$Q = \frac{\Delta G_1^* + \Delta G_0^*}{2}. \quad (B6)$$

Assuming that  $Q$  is  $\gg \Delta G(\xi, T)$ , then for small  $\Delta G(\xi, T)$  Equation (B5) reduces to:

$$R_{degradation} \cong \nu_0 \frac{\Delta G(\xi, T)}{K_B T} \exp\left(-\frac{Q}{K_B T}\right). \quad (B7)$$

For large values of  $G(\xi, T)$  (on the same order of magnitude as  $Q$ ), Equation (B5) reduces to:

$$R_{degradation} \cong \nu_0 \exp\left(-\frac{Q - \Delta G(\xi, T)}{K_B T}\right). \quad (B8)$$

For intermediate values of  $\Delta G(\xi, T)$ , a power law is a reasonable approximation to bridge the gap between low stress (Equation (B7)) and high stress (Equation (B8)).

$$R_{degradation} \cong \nu_0 \left(\frac{\Delta G(\xi, T)}{K_B T}\right)^m \exp\left(-\frac{Q}{K_B T}\right). \quad (B9)$$