



## Viewpoint Paper

## Anti-thermal behavior of materials

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**Abstract**—Thermally activated processes such as diffusivity, grain growth, oxidation, and catalysis are often modeled using the Arrhenius equation, in which the steady-state process rate increases with increasing temperature, yielding a positive activation energy. However, in some systems, the process rate is constant or decreases with increasing temperature. Mechanistic explanations for many types of anti-thermal behavior are lacking. By learning how to control anti-thermal behavior, major advances are possible in fields ranging from catalysis to nanocrystalline alloys to high efficiency engines.

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## 1. Introduction

The assumption of thermally activated behavior is almost ubiquitous in materials science. Accordingly, many processes such as diffusion, grain growth, sintering, creep, oxidation, and catalysis are analyzed using the Arrhenius equation:

$$R = R_0 \exp(-Q/k_B T)$$

where  $R$  is the steady-state rate of the process,  $Q$  is the activation energy,  $k_B$  is Boltzmann's constant,  $T$  is temperature, and  $R_0$  is a constant prefactor related to attempt frequency,  $\nu$ . In addition to describing the functional form of the temperature dependence of the process, this analysis is frequently used to extract a numerical value for the activation energy  $Q$  in order to determine the underlying mechanism (e.g., [1–4]).

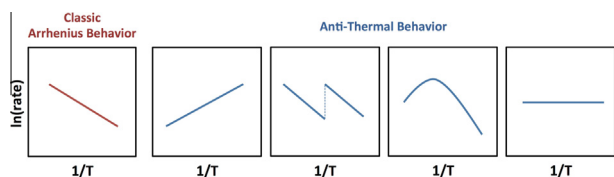
The rates of many processes increase with temperature and accordingly the activation energy  $Q$  obtained from the Arrhenius equation is positive. However, some processes become slower, or do not change at all, as the temperature increases. These processes can be collectively referred to as *anti-thermal*. A schematic diagram illustrating the difference between classic Arrhenius behavior and several types of anti-thermal behavior is shown in Figure 1.

Anti-thermal behavior is often regarded an anomaly or a mere curiosity. The validity of such data might even be questioned, which may explain why there are relatively few reports of anti-thermal behavior in the literature. Rather than being anomalous or mysterious, however, anti-thermal processes have underlying mechanisms that can explain their unusual temperature dependence. The main mystery is learning how to control these underlying mechanisms to engineer and design next-generation materials that break through current temperature barriers. For example, in turbine engines and other high-temperature engineering systems, thermally activated degradation processes such as oxidation and corrosion place an upper limit on the operating temperature, limiting peak efficiency and service life [5]. What if it were possible to apply the mechanistic understanding of anti-thermal behavior to engineer new materials in which diffusion, oxidation, creep, and corrosion actually *decrease* with increasing temperature? The study of anti-thermal behavior offers great opportunity for fundamental research and scientific progress, but there are many challenges that must be met to achieve these advancements.

## 2. Mechanisms of anti-thermal behavior

An example of anti-thermal behavior with which all materials scientists are familiar is electrical conductivity.

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**Figure 1.** The rate of a classic Arrhenius process increases with temperature (left). In contrast, the rate of anti-thermal processes (right) may decrease with temperature continuously (or discontinuously) or may be independent of temperature.

The electrical conductivity of metals decreases with increasing temperature, while the opposite is true for semiconductors. It could be said that metallic conductivity exhibits anti-thermal behavior.

Another example of anti-thermal behavior is retrograde solubility. In systems that exhibit a retrograde solidus line, alloys melt as the temperature is decreased and, conversely, solidify as the temperature increases. This behavior occurs because the maximum solubility of the solute occurs at a temperature higher than the nearby invariant temperature, e.g., above the eutectic temperature. Retrograde solubility occurs in binary alloys of silicon with many different solutes [6], Cu–Bi [7], Al–Sn [8], and numerous other systems [9]. Although not explicitly a rate process, retrograde solubility plays an important role in materials engineering and is integral to other types of anti-thermal behavior which will be discussed later [10].

Mechanistic explanations of anti-thermal behavior for electrical conductivity and retrograde solubility are known, so neither behavior is deemed anomalous. In other words, anti-thermal behavior in materials is only mysterious if the mechanism is not understood. However, many unexplained examples of anti-thermal behavior remain and represent excellent opportunities for research and technological advancement.

### 3. The fallacy of the activation energy

The first step toward discovering the mechanisms of anti-thermal behavior is to accept that the experimental activation energy,  $Q$ , of a given process can be misleading. The Arrhenius equation was originally developed for chemical reactions in which reactants transform into products via a single activated state. This assumption typically means that the Arrhenius equation is most appropriate for reactions in gas and liquid phases. Although the Arrhenius equation is commonly applied to solid-state reactions, its application to these processes has been criticized on practical and theoretical grounds [11–17]. In particular, the application of the Arrhenius equation to precipitation processes, including nucleation, growth, and phase transformation kinetics, has been criticized as yielding activation energies that do not bear any discernable relationship to the underlying mechanisms, and “should be terminated on the ground that not only are the results meaningless but also can be readily misleading” [17]. Even proponents of using the Arrhenius equation to study solid-state processes recognize its shortcomings [18,19].

A fundamental problem with applying the Arrhenius equation to solid-state materials processes is that many of these processes are not elementary reactions with a single activated state and activation energy. Rather, they typically

involve many different reaction pathways each with its own activation energy. In other words, the simple textbook picture of a single activated state between two energy minima does not apply to these processes. Moreover, these different reaction pathways can have opposite temperature dependencies, which further obscures the underlying mechanism [17]. When the Arrhenius equation is applied to such multi-step processes, it yields an *effective* or *apparent* activation energy and pre-exponential term [19]. These experimental values merely describe the temperature dependence of the process within the range of experimental temperatures that were used. Mechanistic explanations cannot be derived from such data.

In extreme cases, the application of the Arrhenius model to solid-state processes yields a negative activation energy, which is inconsistent with the definition of the activation energy. A negative activation energy suggests that the activated state has lower free energy, thus is more stable, than the equilibrium state. Hence, by itself, a negative activation energy cannot offer any mechanistic insight other than to rule out a single activated state. Processes with apparent negative activation energies are often called “anti-Arrhenius.”

There are also solid-state processes that may be temperature-dependent, but in a non-Arrhenius manner. One well-known example is the barrier-free phase transformation [20]. True non-thermally activated processes are referred to as “non-Arrhenius”, which should be distinguished from *apparent* non-Arrhenius processes (with an effective activation energy equal to zero).

What can be learned from an apparent activation energy derived from experiment? It cannot be used to determine mechanisms. It simply describes the temperature dependence of the combined rate processes *under a particular set of experimental conditions*. To illustrate this important point, let us consider apparent activation energies from experimental studies on nanocrystalline grain growth. It is common practice to use the apparent activation energy of grain growth to suggest a growth mechanism [1]. Since nanocrystalline grain growth often has a different apparent activation energy than grain growth in coarse-grained polycrystals, it is often believed that the grain growth mechanisms are different. For example, the activation energy for grain growth in nanocrystalline Fe was reported as 125 kJ/mol, 248 kJ/mol, and 330 kJ/mol depending on the temperature regime [2,21], compared to grain growth in coarse-grained iron with an apparent activation energy of 249 kJ/mol [22]. Activation energies higher and lower than that in coarse-grained polycrystals were taken as evidence that a mechanism unique to nanocrystalline materials controls grain growth. This conclusion is inconsistent with recent experiments that show that average grain boundary diffusivity, and the associated activation energy, are grain size-independent down to the nanoscale [23]. The large spread in measured activation energies, their dependence upon temperature regime, the fact that nanocrystalline materials evince both lower and higher activation energies compared to coarse-grained materials, and the contradictory experimental evidence all suggest that the activation energy by itself is not very useful for understanding the mechanisms of nanocrystalline grain growth.

The same problems occur with virtually every attempt to use the apparent activation energy to determine underlying process mechanisms. For example, an activation energy of 1.2 eV/atom (approximately 120 kJ/mol) is typical for low

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