

Determination of Activation Energies Using the Atlas S³T-System*

*Specimen Specific Surface Temperature System

Introduction

The surface temperature is a crucial factor influencing photochemical and weathering processes. The temperature dependence of chemical reaction rates can be estimated using the Arrhenius equation, which can be modified also for photochemical degradation reactions (Equation 1):

$$k = A \cdot E_{eff}^{\alpha} \cdot e^{-\frac{E_a}{RT}} \quad (\text{Equation 1}).$$

Here

k is the reaction rate constant,
 A is the Arrhenius factor,
 R is the universal gas constant (8.314 J·Mol⁻¹·K⁻¹),
 T is the absolute temperature (in K),
 E_a is the activation energy (in J·mol⁻¹) of the considered property change,
 E_{eff} is the effective irradiance and
 α is a material-specific coefficient.

Due to the lack of a specific traceable chemical parameter or reaction during a weathering test, usually a specific macroscopic property change (such as gloss loss or color change) is considered for the Arrhenius equation. Some limitations apply by using this chemical concept on material degradation.

Theoretical Acceleration Factors

The lifetime based on an accelerated test is the reaction rate constants under accelerated (a) and use (u) conditions (Equation 2):

$$\frac{k_a}{k_u} = \left(\frac{E_{eff,a}}{E_{eff,u}} \right)^{\alpha} \cdot e^{\frac{E_a}{R} \left(\frac{1}{T_u} - \frac{1}{T_a} \right)} = AF_R \cdot AF_T = AF \quad (\text{Equation 2}).$$

AF is the general acceleration factor;
 AF_T is a temperature-related acceleration factor and
 AF_R is the radiation-induced theoretical acceleration factor.

For the lifetime estimation of opaque samples, the surface temperature should be selected. Other factors that influence the photodegradation are the effective irradiance [1, 2] and the oxygen concentration, which typically have their maximum at the sample surface and decrease with distance from the surface [3].

Determination of activation energies

For service life estimations taking into account the temperature influence on degradation, the activation energy of the degradation process needs to be known. This requires experiments to be conducted at different temperatures under otherwise identical conditions, on acceptance that the activation energy is temperature independent within small temperature ranges.

Individual weathering tests have to be performed until a certain property change appears, or for a fixed period of time, at a minimum of two different temperatures (for example, at standard conditions and at ± 5 K black standard or black panel temperature at standard conditions). All other parameters (irradiance, relative humidity, cycle parameters) must be kept constant and the sample temperature has to be measured. The S³T system is a convenient tool here allowing the continuous measurement of the surface temperature of multiple samples in different colors without special sample preparation (Note: Under varying conditions, the so-called effective temperatures must be calculated in order to determine the activation energy [1, 2]).

The activation energy can be calculated on the basis of two weathering tests according to the logarithmic Arrhenius equation (Equation 3), or graphically determined on the basis of two or more weathering tests. When the natural logarithm of k is plotted versus the inverse of the temperature ($1/T$), the slope is a straight line with a value equal to $-E_a/R$ (according to Equation 4, Figure 1):

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{(Equation 3)}$$

$$\ln(k) = \ln(A \cdot E_{\text{eff}}^\alpha) - \frac{E_a}{R} \cdot \frac{1}{T} \quad \text{(Equation 4)}$$

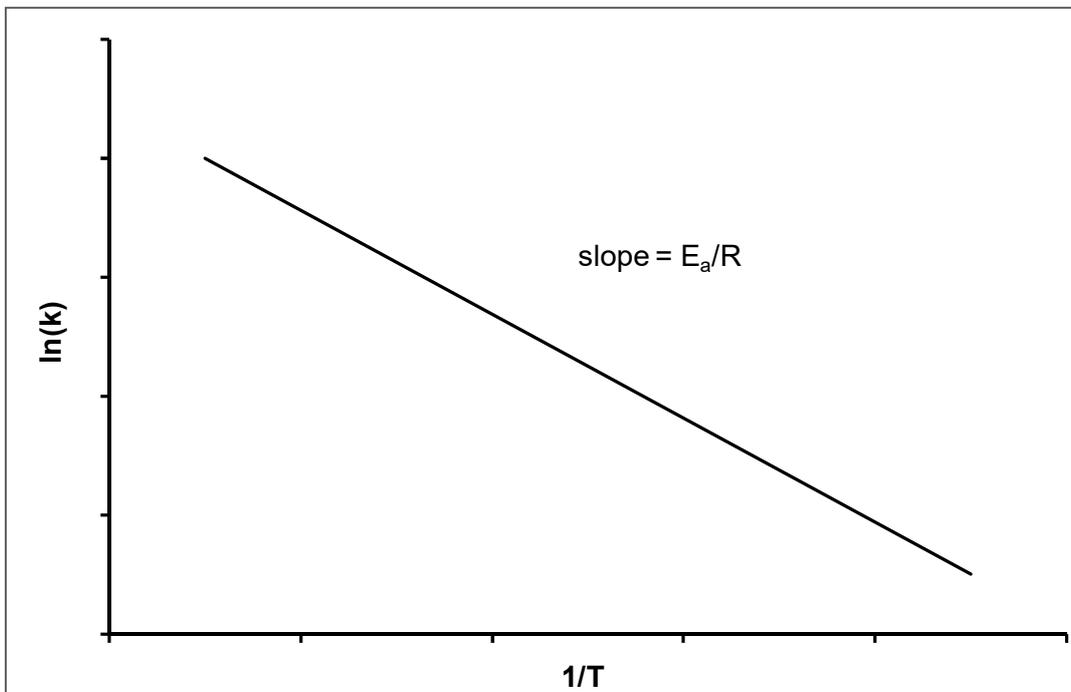


Figure 1: Graphical determination of the activation energy according to Eq. 4.

Depending on polymer and the degradation process the activation energies of the photodegradation of polymeric materials range usually from 10 and 100 kJ·mol⁻¹ [e.g. 1, 4, 5]. However, the number of relevant publications is limited, since the accurate determination of activation energies on weathering and photodegradation of polymers and coatings can be very time-consuming and complicated. If weathering experimenters are willing to invest the effort to make a proper determination of activation energies, it will be valuable to take the actual sample surface temperatures into account and not rely on rough estimates based on reference temperatures.

References

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