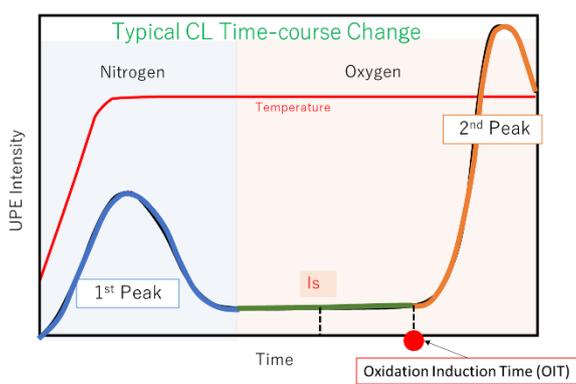


## Calculation of Activation Energy by Chemiluminescence (2)

### Introduction

Upon stimulation by, for example, heat or light, an unoxidised sample (RH) produces R· radicals which react with oxygen to form peroxides (ROOH) through multiple reactions. The peroxides accumulate inside the sample or further decompose to produce the next radical reaction, and oxidation proceeds automatically. Because the RC=O\* (excited carbonyl) produced by the bimolecular reaction of the ROO· radicals produced in this process generates light when falling from the excited state to the ground state, the progress of the oxidation reaction can be measured from the change in intensity of the weak luminescence in the oxidation reaction.



The graph on the left shows typical CL behaviour during heating measurement. As the sample is heated, the peroxide decomposes, and CL from the excited carbonyl increases, resulting in a peak (the first peak). This corresponds to the amount of peroxide at that point.

The oxidation reaction is then accelerated by heating in air or oxygen, and eventually the CL reaches a state of equilibrium. The intensity at this time is termed the steady-state luminous intensity (**Is**). In the sample to which stabiliser has been added, the stabiliser is consumed, the steady state of the oxidation reaction is disrupted, and the amount of radicals in the sample increases, resulting in the appearance of significantly higher luminescence (the second peak). This point is called **the oxidation induction time (OIT)**. Using the OIT, the oxidative stability of the sample can be evaluated. Also, since **Is** is the steady state of radical extinction and generation within the sample, it represents the rate of radical generation, and this value can also be used to evaluate the oxidative stability of the sample.

In thermal analysis, a method of predicting lifespan has been reported, whereby the activation energy at each temperature is determined from the temperature dependence of the peak exothermic time of the isothermal measurement. The Arrhenius equation for activation energy calculation expresses the speed of the chemical reaction at a certain temperature T, and shows that “the speed of many chemical reactions increases exponentially as the temperature rises”. This also applies to the speed at which materials deteriorate (oxidise), and is also used as the basis for raising the temperature to shorten the test time in durability testing of various industrial products.

$$\text{Arrhenius equation} \quad k = A \exp\left(-\frac{E_a}{RT}\right)$$

K: rate constant, A: frequency factor, Ea: activation energy [eV],  
R: Boltzmann's constant ( $8.6173 \times 10^{-5}$  [eV/K]), T: absolute temperature [K]

Therefore, an attempt was made here to calculate the activation energy using **Is**.

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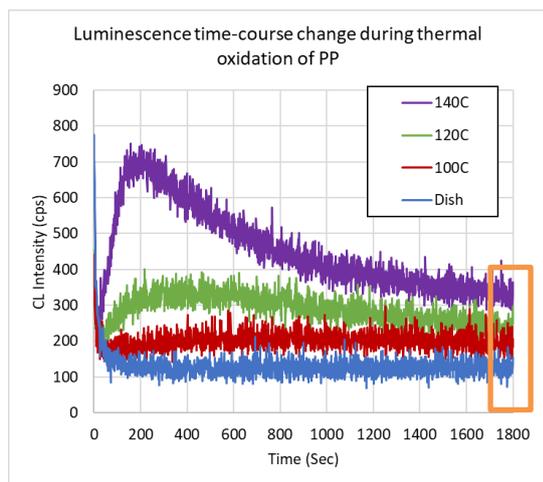
TOHOKU 東北電子産業株式会社

Tohoku Electronic Industrial Co., Ltd.

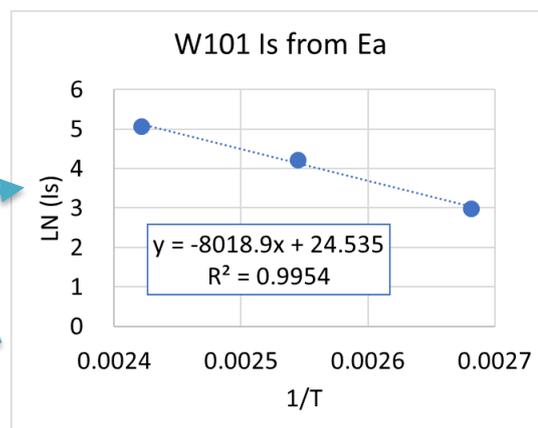
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**Measurement example**

Samples	200Mg W1010 polypropylene (PP) pellets, Sumitomo chemical Co., Ltd.
Measurement devices	Main unit: CLA-FS4; sample chamber: CLS-ST4; both manufactured by Tohoku Electronic Industrial Co., Ltd.
Measurement procedure	The samples were positioned in the sample chamber, set to each temperature (100°C, 120°C and 140°C), and Is was measured under oxygen flow (average for 1,741 to 1,800 seconds).



	100°C	120°C	140°C
1/T	0.00268	0.00254	0.00242
Is	191.62	239.12	331.73
Dish subtraction	20.05	67.55	160.17
LN (Is)	3.00	4.21	5.08



	100-140sec (after subtraction)
Slope	-8018.8
Gas constant	-8.3147
Ea	66.7

Result: Activation energy was calculated to be 66.7kJ/mol.

This method requires at least 3 sets of temperature conditions, but because the CL method has high sensitivity, measurement can be performed at temperatures low enough for the samples not to melt, and in addition, Ea can be calculated in a relatively short measurement time of about 30 minutes per sample. As one of the indices of oxidation stability, Ea can be used for purposes including evaluation of oxidation stabilisers, evaluation of oxidation stability in the development of new materials, and lifespan prediction.

Samples supplied by: Petrochemicals Research Laboratory, Sumitomo Chemical Co., Ltd.

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