

# 04B: Arrhenius Temperature Dependence

$$\dot{\epsilon} = A \frac{\sigma^n}{d^p} e^{-\frac{Q}{RT}}$$

## Temperature Dependence: Arrhenius Equation and the Activation Energy

Let us consider Eq. 3 again

$$\log_{10} \dot{\epsilon} = \log_{10} A + n \log_{10} \sigma - \frac{Q}{2.3RT} - p \log_{10} d \quad (3)$$

The temperature dependence is contained in this term

$$\frac{Q}{2.3RT} \quad (4)$$

$Q$  is called the activation energy, usually in units of  $\text{kJ mol}^{-1}$ .

$R = 8.31 \text{ J mol}^{-1}\text{K}^{-1}$  it is called the Gas Constant defined by the ideal gas law  $PV = nRT$

$T$  temperature in Kelvin (K)

Note that Eq. (4) is dimensionless.

The temperature dependence of the strain rate. Let us rewrite Eq. (1) in the following form

$$\dot{\epsilon} = \dot{\epsilon}_o e^{-\frac{Q}{RT}} \quad (5)$$

where  $\dot{\epsilon}_o = A \frac{\sigma^n}{d^p}$

Note that  $\dot{\epsilon}_o$  is independent of temperature; it is generally called the pre-exponential.

The form of Eq. (5) is generally known as the Arrhenius equation. It is characterized by: (i) a pre-exponential, and (ii) temperature dependent exponential term, which is characterized by  $Q$ , which is called the activation energy.

## Significance of Q, the Activation Energy

The activation energy is a fundamental material parameter, that is, it has a characteristic value for different materials. It refers to the mechanism of solid-state diffusion which we shall discuss later. Solid-state diffusion can occur by two different mechanisms: (i) through the crystal lattice, and (ii) along the grain boundary. They are called as volume or lattice diffusion, written as  $D_V$ , and boundary diffusion written as  $D_B$ , each with their own activation energy. The coefficient of solid-state diffusion which measured the rate of transport of atoms in the solid state has a form that is equivalent to Eq. (5), that is

$$D = D_o \exp \frac{Q}{RT}$$

The activation energy for lattice diffusion is different than for grain boundary diffusion.

Now, to obtain a value for  $Q$  from experimental data we consider a logarithmic form of Eq. (5):

$$\log_{10}(\dot{\epsilon}) = \log_{10}(\dot{\epsilon}_o) - \frac{Q}{2.3RT} \quad (6A)$$

Since the activation energy is usually expressed in  $\text{kJ mol}^{-1}$  and the temperature is usually in the  $500\text{ }^\circ\text{C}$  to  $2000\text{ }^\circ\text{C}$  range is more convenient to write (6A) as follows

$$\log_{10}(\dot{\epsilon}) = \log_{10}(\dot{\epsilon}_o) - \frac{1}{2.3R} \cdot \frac{Q}{1000} \cdot \frac{1000}{T} \quad (6B)$$

A plot of the left-hand side vs  $(1000/T)$  is shown in the schematic in Fig. 3, on the following page. Further simplifying Eq. (6B) to measure the value for  $Q$

$$\frac{Q}{1000} (\text{units of } \text{kJmol}^{-1}) = -2.3 R \frac{\Delta(\log_{10} \dot{\epsilon})}{\Delta\left(\frac{1000}{T(K)}\right)} \quad (6C)$$

where  $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ .

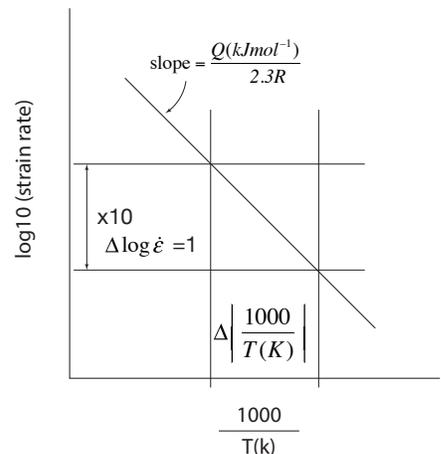
The method for obtaining the value for  $Q$  in units of  $\text{kJ mol}^{-1}$  is to take one (or you may consider two orders of magnitude) spread of the strain rate and obtain the corresponding spread in  $(1000/T)$  on the horizontal axis. Substituting these values into Eq. (6C) will yield the activation energy.

### Creating a template for the Arrhenius Plot.

Considerations:

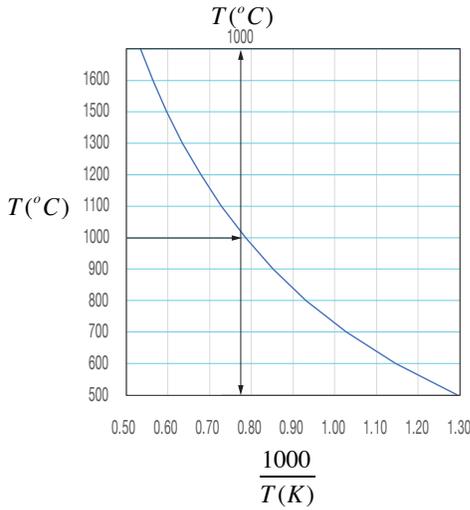
$$\text{Slope} = \frac{\Delta \log \dot{\epsilon}}{\Delta \left[ \frac{1000}{T(K)} \right]} \quad Q(\text{kJ mol}^{-1}) = 2.3R \frac{(\Delta \log \dot{\epsilon})}{\Delta \frac{1000}{T}}$$

Figure 3



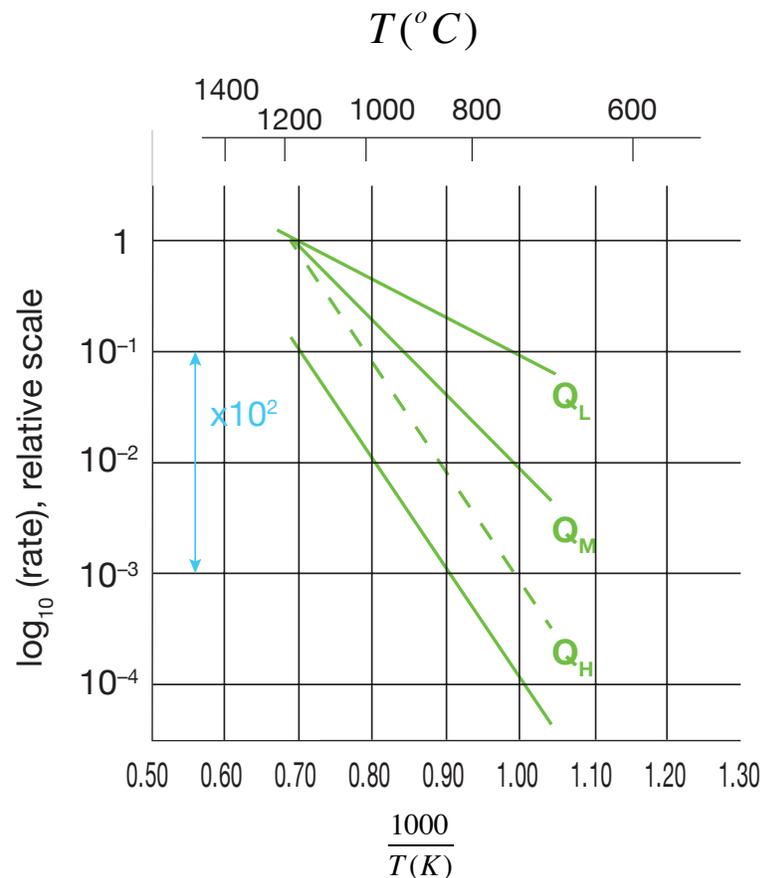
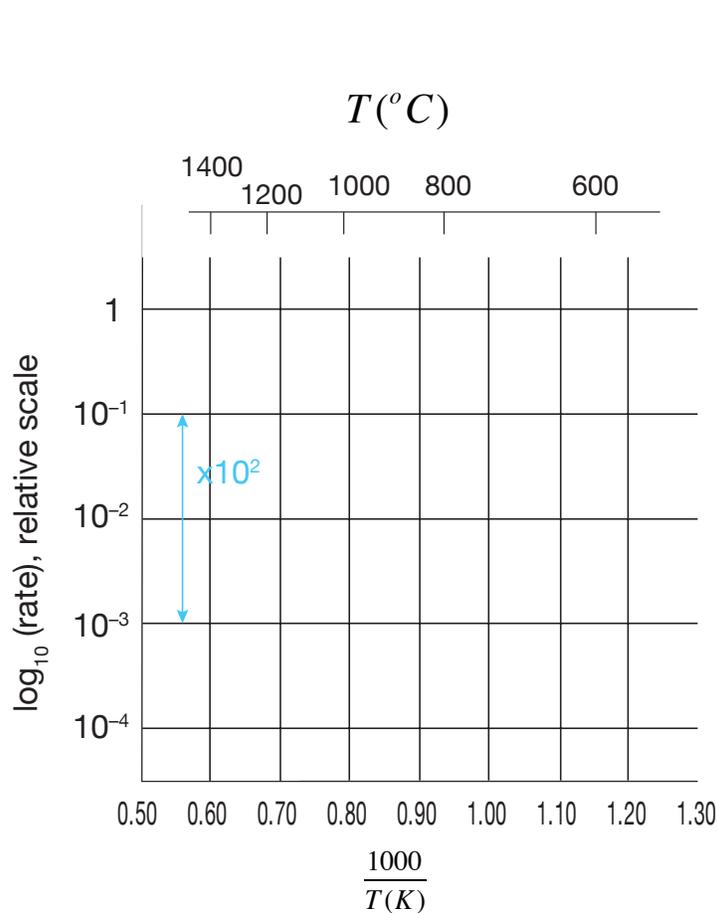
•The rate axis (the vertical axis) is relative since we are interested in the relative ratio of the rates when the temperature is increased.

•However, the temperature scale covers a specific range of temperature (let us consider the range of 1150 to 1450 °C as given by the data in Fig. 2. Let us convert this temperature range into a range for (1000/T(K))



500	773	1.29
600	873	1.15
700	973	1.03
800	1073	0.93
900	1173	0.85
1000	1273	0.79
1100	1373	0.73
1200	1473	0.68
1300	1573	0.64
1400	1673	0.60
1500	1773	0.56
1600	1873	0.53

Which then leads to the following template for analyzing the data for the activation energy.



Notes:

- i. The strain rate axis uses a logarithmic scale to the base "10", which means that each unit is equal to a factor of 10. Usually, in publications and in books, the legend does not specify the logarithmic scale. It is garnered from the values of the units that is  $10^{-2}$ ,  $10^{-1}$ , etc. rather than a linear scale of 1, 2, etc. The factor of ten increment at each step implies a base 10 for the logarithmic scale.
- ii. Note how the real temperature scale shown at the top stretches out at lower temperatures, and compresses at higher temperatures, the implication being that the strain rate changes more quickly at higher temperatures.
- iii. The "idealized" straight line fits to data in the Arrhenius plots arise from  $\dot{\epsilon} = \dot{\epsilon}_o e^{-\frac{Q}{RT}}$ , where  $\dot{\epsilon}_o = A \frac{\sigma^n}{d^p}$ . Therefore, the slope of the lines remains the same for plots made for different values of stress (again, to emphasize the slope is related to the activation energy  $Q$ . The intercept on the y-axis moves to a higher strain rate as the stress increases (or the grain size decreases).
- iv. The logarithmic scale is converted into actual values by using  $10^x$  for  $\log_{10}(x)$ . So for example if one unit on the log scale is 100 points long then 50 points, or one half the length of one unit will be equivalent to a factor of  $10^{0.5} =$  factor of 3.16 starting from 1. If starting from 0.1, then it would be 0.316, and so on.