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Chem 501

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A picture of Svante Arrhenius borrowed from www.britannica.com/.../Svante-Arrhenius-1918

Arrhenius Kinetics Verification

In 1889 Sweedish chemist Svante Arrhenius developed the equation named after him (Eq. 1).

$$k = Ae^{\frac{-E_A}{RT}}$$ (1)

This equation shows how the rate constant, k, is affected by the absolute Kelvin temperature. It also includes the activation energy of the reaction, E_A; the thermodynamic gas constant, R; and a frequency factor which describes the probability a reaction will occur based on molecular orientation, A. Arrhenius used five sets of reaction-rate data from other scientists to develop his equation. One set of data was obtained from the reaction between ethoxide and methyliodide (Fig. 1). This reaction was studied by Hecht and Conrad in 1889.
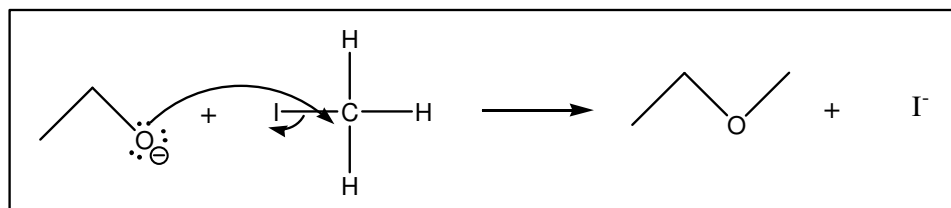

FIGURE 1 The reaction between ethoxide and methyliodide to form ethyl, methyl ether and the iodide ion.

A plot of reaction rate, k, versus absolute temperature reveals an exponential curve (Fig. 2). This graph is not very useful because it implies that $-\frac{E_A}{R}$ is 0.120. Since R is constant and positive, the activation energy would have to be negative. Activation energies are positive.
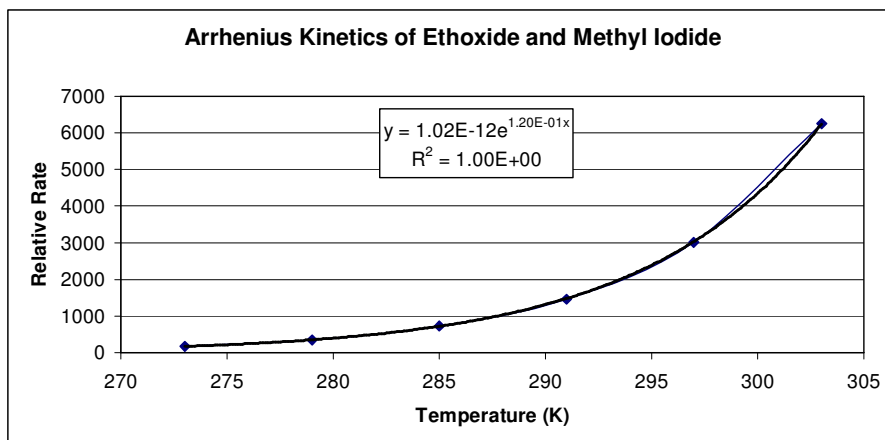
FIGURE 2 The plot of rate versus absolute temperature for the Hecht and Conrad experiment.

A more useful plot is where the natural log of the rate is plotted versus the inverse
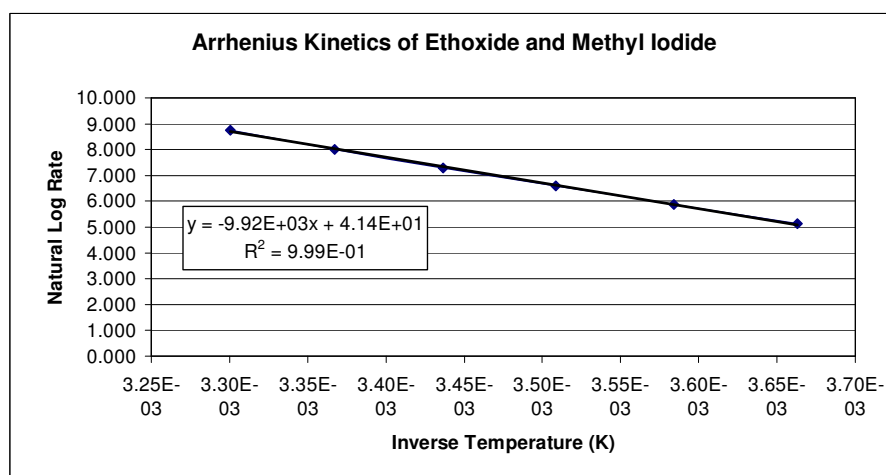
temperature (Fig. 3).

FIGURE 3 The plot of ln(rate) versus inverse (absolute temperature) for the Hecht and Conrad experiment.

Taking the natural log of Arrhenius' equation yields the equation for the line in Figure 3

(Eq. 2). The slope is equal to $\dfrac{-E_A}{R}$ and the y-intercept is the ln(A). Solving for the activation

energy by using the slope for the line in Figure 3 yields 82.5kJ/mol.

$$\ln(k) = \frac{-E_A}{R}\frac{1}{T} + \ln(A) \tag{2}$$

It is interesting to note that the ln(k) versus $\frac{1}{T}$ plot is not the only straight-line plot for

the data. The ln(k) versus the ln(T) plot (Fig. 4) and the ln(k) versus T plot (Fig. 5) are also

linear. It is not clear to me why this is significant and if the slopes or intercepts for these graphs
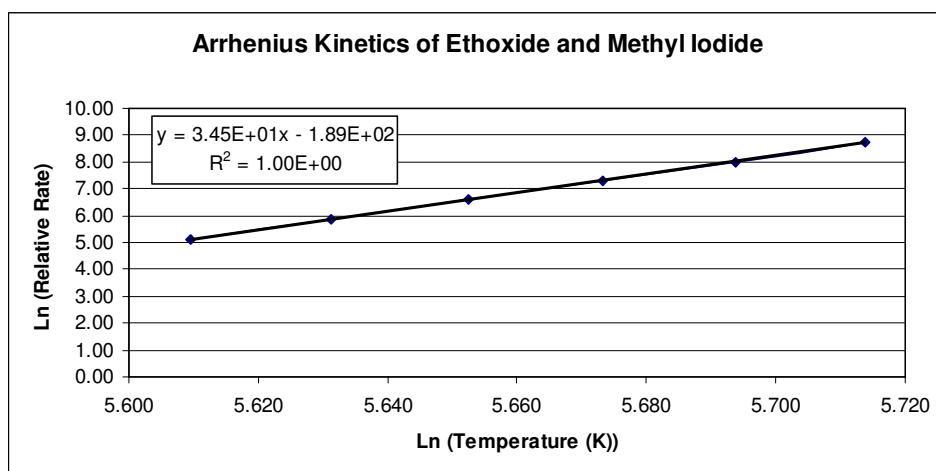
are of any physical value.

Arrhenius Kinetics of Ethoxide and Methyl Iodide

y = 3.45E+01x - 1.89E+02
R^2 = 1.00E+00

Ln (Relative Rate) vs Ln (Temperature (K))

FIGURE 4 The plot of ln(rate) versus ln(temperature) for the Hecht and Conrad experiment.

Arrhenius Kinetics of Ethoxide and Methyl Iodide

y = 1.20E-01x - 2.76E+01
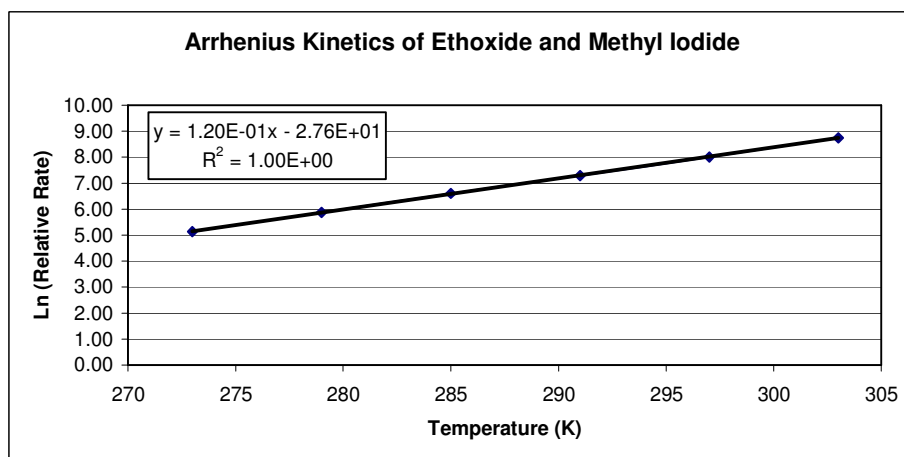R^2 = 1.00E+00

Ln (Relative Rate) vs Temperature (K)

FIGURE 5 The plot of ln(rate) versus temperature for the Hecht and Conrad experiment.