

SAMPLE EXERCISE 14.8

The following table shows the rate constants for the rearrangement of methyl isonitrile at various temperatures (these are the data that are graphed in Figure 14.6).

Temperature (°C)	k (s ⁻¹)
189.7	2.52×10^{-5}
198.9	5.25×10^{-5}
230.3	6.30×10^{-4}
251.2	3.16×10^{-3}

(a) From these data calculate the activation energy for the reaction. (b) What is the value of the rate constant at 430.0 K?

SOLUTION (a) We must first convert the temperatures from degrees Celsius to kelvins. We then take the inverse of each temperature, $1/T$, and the natural log of each rate constant, $\ln k$. This gives us the following table:

T (K)	$1/T$ (K ⁻¹)	$\ln k$
462.9	2.160×10^{-3}	-10.59
472.1	2.118×10^{-3}	-9.85
503.5	1.986×10^{-3}	-7.37
524.4	1.907×10^{-3}	-5.76

A graph of $\ln k$ versus $1/T$ results in a straight line, as shown in Figure 14.12. The slope of the line is obtained by choosing two well-separated points, as shown, and using the coordinates of each:

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{-6.6 - (-10.4)}{0.00195 - 0.00215} = -1.9 \times 10^4$$

Because logarithms have no units, the numerator in this equation is dimensionless. The denominator has the units of $1/T$, namely, K⁻¹. Thus, the overall units for the

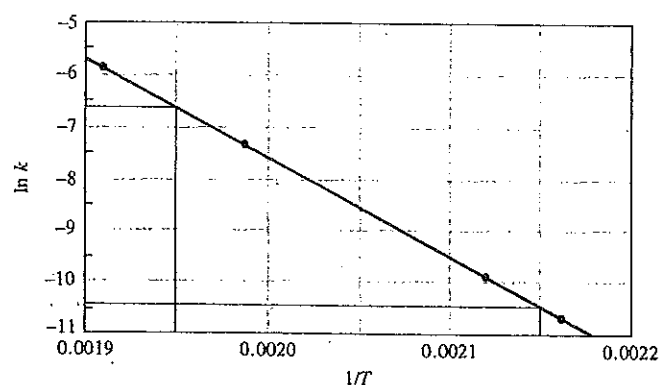


FIGURE 14.12
The natural logarithm of the rate constant for the rearrangement of methyl isonitrile as a function of $1/T$. The linear relationship is predicted by the Arrhenius equation.

slope are K. The slope is equal to $-E_a/R$. We use the value for the molar gas constant R in units of J/mol-K (Table 10.2). We thus obtain

$$\begin{aligned} \text{Slope} &= -\frac{E_a}{R} \\ E_a &= -(\text{slope})(R) = -(-1.9 \times 10^4 \text{ K}) \left(8.31 \frac{\text{J}}{\text{mol-K}} \right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) \\ &= 160 \text{ kJ/mol} \end{aligned}$$

Note that we report the activation energy to two significant figures; we are limited by the precision with which we can read the graph in Figure 14.12.