

Extra Credit Worksheet (Maximum number of points you can get is 5 pts)

1. (2 pts) The water flea *Daphnia* performs a constant number of heart beats and then dies. The flea lives twice as long at 15°C as at 25°C. Calculate the activation energy for the reaction that controls the heart beat.

$$T_1 = 15^\circ\text{C} = 288.15\text{ K} ; T_2 = 25^\circ\text{C} = 298.15\text{ K}$$

$$k = A e^{-E_0/RT} \Rightarrow \ln k = \ln A - E_0/RT$$

$$v[T_1] = \frac{1}{2} v[T_2] \Rightarrow k_1 = \frac{1}{2} k_2 \Rightarrow k_2 = 2k_1$$

$$\Rightarrow \ln \frac{k_2}{k_1} = \ln 2 = -\frac{E_0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = -\frac{E_0}{R} \frac{T_1 - T_2}{T_1 T_2} = E_0 \frac{T_2 - T_1}{R T_1 T_2}$$

$$\Rightarrow E_0 = \ln 2 \cdot R T_1 T_2 / (T_2 - T_1) = 0.6932 \cdot 8.3145 \cdot \frac{288.15 \cdot 298.15}{10} \text{ J/mol}$$

$$= 0.6932 \cdot 8.3145 \cdot 8591.27 = 49516 \text{ J/mol} = 49.5 \text{ kJ/mol}$$

2. (2 pts) The thermal denaturation of a substance A is a first-order process. Its half-life time has been found 4000 s at $T_1=300\text{ K}$, and 500 s at $T_2=400\text{ K}$. Calculate its activation energy E_a in kJ/mol

$$t_{1/2} = \ln 2 / k \Rightarrow k = \ln 2 / t_{1/2} \Rightarrow k_1 = 1.39 \cdot 10^{-3} \text{ s}^{-1} ; k_2 = 1.73 \cdot 10^{-4} \text{ s}^{-1}$$

$$k = A \cdot e^{-E_0/RT} \Rightarrow \ln k = \ln A - E_0/RT$$

$$\Rightarrow \ln k_1 - \ln k_2 = \ln \frac{k_1}{k_2} = -\frac{E_0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = -\frac{E_0}{R} \frac{T_2 - T_1}{T_1 T_2}$$

$$\Rightarrow E_0 = R \cdot \ln \frac{k_1}{k_2} \cdot \frac{T_1 T_2}{T_2 - T_1}$$

$$= 8.3145 \cdot \ln 18 \cdot \frac{300 \cdot 400}{100} \text{ J/mol}$$

$$= 8.3145 \cdot 2.079 \cdot 1200 \text{ J/mol} = 20743 \text{ J/mol} = 20.7 \text{ kJ/mol}$$

3. (1 pt) What is the relation between rate constants k_{ir} and k_{re} and equilibrium concentrations [A] and [B] for a reaction $A \rightleftharpoons B$.

$$\text{In equilibrium: } k_{ir} [A]_{eq} = k_{re} [B]_{eq}$$

$$\Rightarrow \frac{k_{ir}}{k_{re}} = \frac{[B]_{eq}}{[A]_{eq}}$$