CHEM 3423 001 Spring 2024 **Name:** KEY
ID:

Worksheet #14 (Total number of **extra credit** points you can get is 3 pts)

1. Two reactions of the same order have identical activation energies. Their entropies of activation differ by 70 J/(K mol). Calculate the ratio of their rate constants at any temperature.

$$k = e^{2} \frac{k_B T}{h} e^{\Delta^{\ddagger} S / R} e^{-E/RT}$$

$$\Rightarrow \frac{k_1}{k_2} = e^{70/R} = e^{8.388} = 4394$$

2. The thermal denaturation of a substance A is a first-order process. Its half-life time has been found 4000 s at T_1=350 K and 500 s at T_2=400 K. Calculate its activation energy E_a.

$$t_{1/2} = \ln 2 / k \Rightarrow k = \ln 2 / t_{1/2} \Rightarrow k_1 = 1.733 \times 10^{-4} \frac{1}{s}; \; k_2 = 1.34 \times 10^{-3} \frac{1}{s}$$

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

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

$$\Rightarrow E_a = R \ln \frac{k_2}{k_1} \cdot T_1 T_2 / (T_2 - T_1)$$

$$= 8.3145 \cdot \ln 8.03 \cdot 2800 \; J/mol$$

$$= 8.3145 \cdot 2.084 \cdot 2800 \; J/mol$$

$$= 48.41 \; kJ/mol$$

3. Assume that the activation energy of problem 2 is related to the enthalpy of activation $\Delta^{\ddagger}H^{\circ}$ by $E_a = \Delta^{\ddagger}H^{\circ} + RT$. Assume the process of problem 2 can be described by the Eyring equation: $k = k_B T/h \exp(-\Delta^{\ddagger}G^{\circ}/RT)$. Calculate the enthalpy of activation and entropy activation at T=350 K.. (k_B=1.3807 x 10^{-23}]/K; h=1.0546x10^{-34}]s).

$$\Delta^{\ddagger}H^{\circ} = E_a - RT = 48.41 \; kJ/mol - 8.3145 \cdot 350 \; J/mol = 45.501 \; kJ/mol$$

$$\Delta^{\ddagger}G^{\circ} = \ln\left(\frac{k_B T}{h k}\right) RT = \ln(2.644 \times 10^{13}) \cdot 8.3145 \cdot 350 \; J/mol$$

$$= 40.118 \cdot 8.3145 \cdot 350 \; J/mol = 116.75 \; kJ/mol$$

$$\Delta^{\ddagger}G^{\circ} = \Delta^{\ddagger}H^{\circ} - T\Delta^{\ddagger}S^{\circ} \Rightarrow \Delta^{\ddagger}S^{\circ} = (\Delta^{\ddagger}H^{\circ} - \Delta^{\ddagger}G^{\circ})/T = -71.15 \; kJ/mol / 350K$$

$$= -203 \; J/molK$$