

Homework 14

1. The entropy change for the "skating molecule" going to vapor (3 degrees of freedom) is less than for tightly bound surface molecule. This lowers A (freq. factor) for the "skater".



b) No -- ΔG^{\ddagger} , ΔH^{\ddagger} and ΔS^{\ddagger} (for the formation of the transition state) changes but NOT ΔG° , ΔH° , ΔS° (implied as being for the reaction. [state variables... path independent!])

c) reactions are slow! (favorable... but slow)

d) collision theory: max cross section; probability of "effective collision" (P); E_a (and μ , reduced mass, to a small degree.

transition state: ΔH^{\ddagger} , ΔS^{\ddagger} , ΔG^{\ddagger} K (transmission coeff; i.e., probability of conversion to product)

HW 14 (cont)

3. Rate $\propto k$ so find change of k with T

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

$$\frac{k_1}{k_2} \approx 12$$

4. Assume that "state of the egg" is the same in both cases (e.g., extent of reax; amnt of "products", etc is the same).

Thus, $t_{\text{cook}} \propto \frac{1}{k}$ (assumes 1st order in "egg")

$$\ln\left(\frac{k_1}{k_2}\right) = \ln\left(\frac{t_2}{t_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a \approx 72 \text{ kJ/mole.}$$

5. Reax rate doubles because k doubles ~~etc~~

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

$$E_a \approx 53 \text{ kJ/mole.}$$