

## 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 --  $\Delta G^{\ddagger}$ ,  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$  (for the formation of the transition state) changes but NOT  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$  (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  $\mu$ , reduced mass, to a small degree.

transition state:  $\Delta H^{\ddagger}$ ,  $\Delta S^{\ddagger}$ ,  $\Delta G^{\ddagger}$   $K$  (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 1<sup>st</sup> 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~~

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

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