Lecture 38 CH102 A1 (MWF 9:05 am)

Wednesday, May 3, 2017

- Rate versus temperature: E_a and A
- Putting it all together: First law, second law, equilibrium, and kinetics.

Rate versus temperature: E_a and A

[TP] When T is increased, the rate of every chemical reaction must...

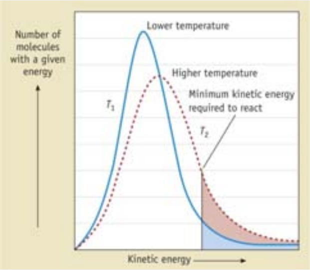
25% 1. increase
25% 2. stay the same
25% 3. decrease
25% 4. More information needed

Response Counter

5

[TP] Rate constants depend on T as $k = A \exp(-E_a / (R T))$
The value of k at $T = 0$ is ...

25% 1. 0
25% 2. A
25% 3. $E_a / (R T)$
25% 4. ∞



Response Counter

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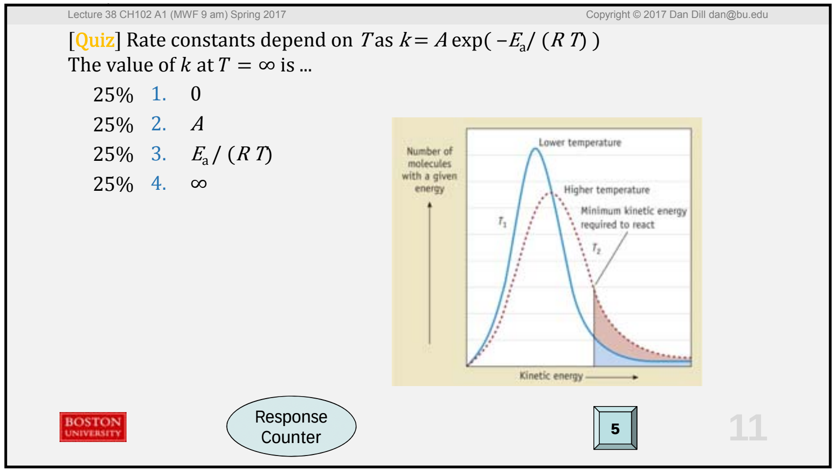

[Quiz] Rate constants depend on T as $k = A \exp(-E_a/(RT))$
The value of k at $T = \infty$ is ...

- 25% 1. 0
- 25% 2. A
- 25% 3. $E_a/(RT)$
- 25% 4. ∞

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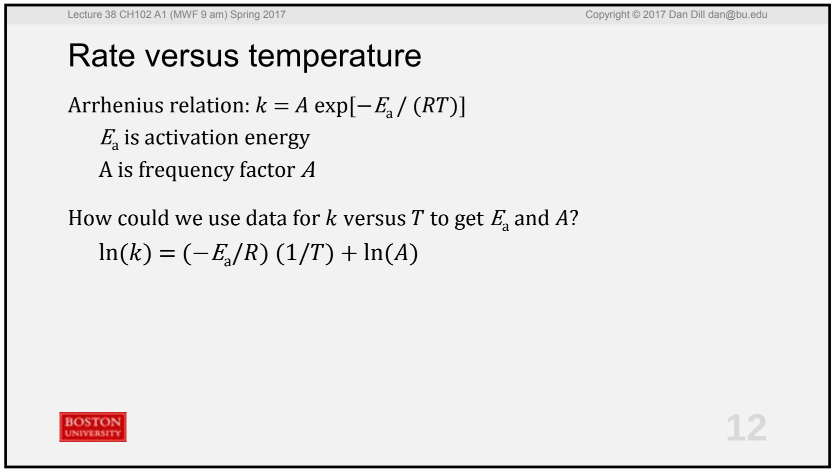
Response Counter

5



Rate versus temperature

Arrhenius relation: $k = A \exp[-E_a/(RT)]$

E_a is activation energy

A is frequency factor A

How could we use data for k versus T to get E_a and A?

$\ln(k) = (-E_a/R)(1/T) + \ln(A)$

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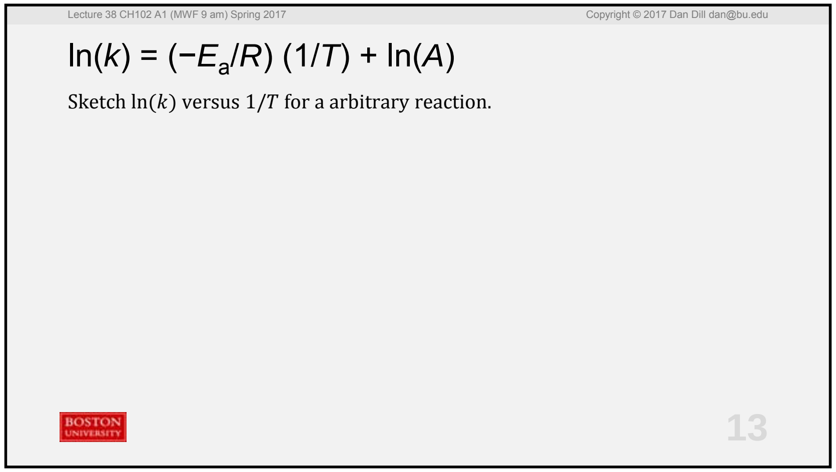

$\ln(k) = (-E_a/R)(1/T) + \ln(A)$

Sketch $\ln(k)$ versus $1/T$ for a arbitrary reaction.

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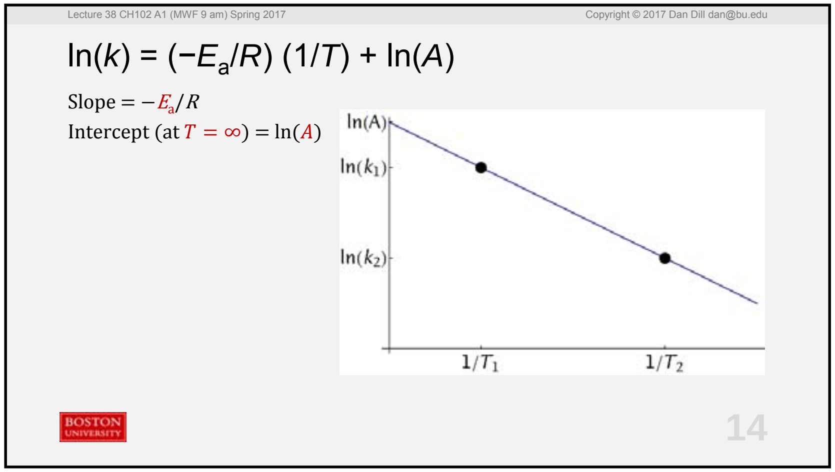

$\ln(k) = (-E_a/R)(1/T) + \ln(A)$

Slope = $-E_a/R$

Intercept (at $T = \infty$) = $\ln(A)$

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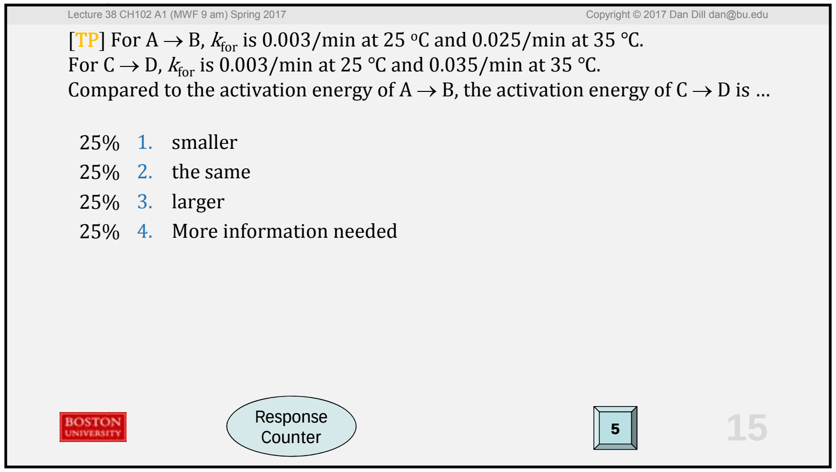
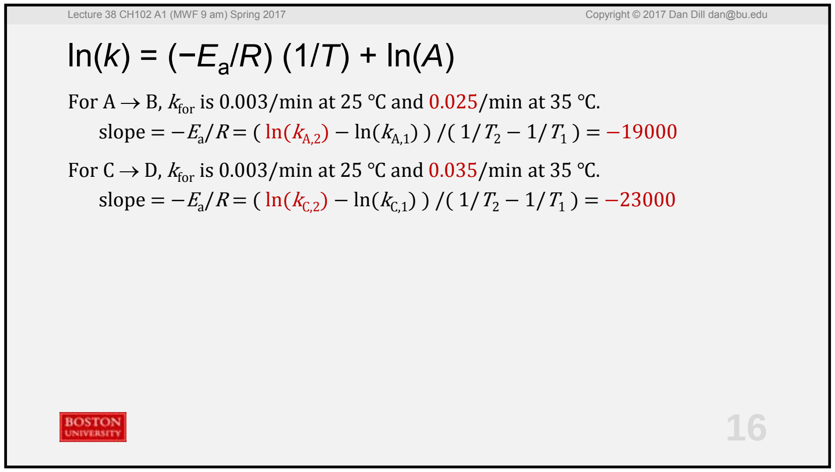


[TP] For A → B, k_{for} is 0.003/min at 25 °C and 0.025/min at 35 °C.
For C → D, k_{for} is 0.003/min at 25 °C and 0.035/min at 35 °C.
Compared to the activation energy of A → B, the activation energy of C → D is …

25% 1. smaller
25% 2. the same
25% 3. larger
25% 4. More information needed

Response Counter

5



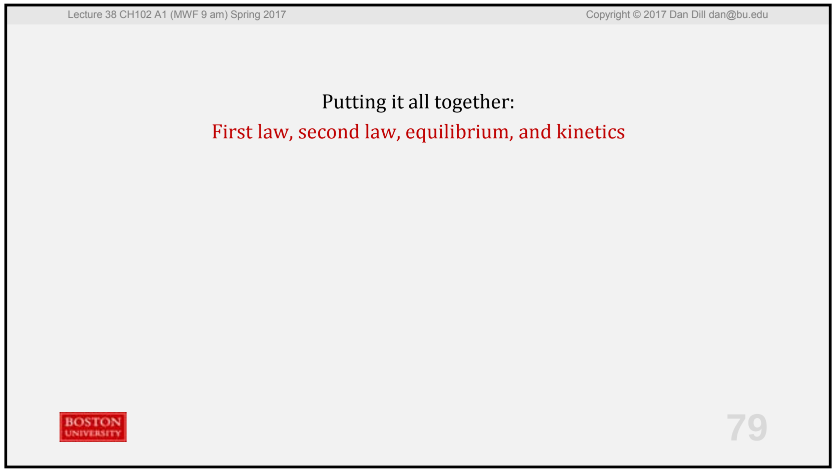
$\ln(k) = (-E_a/R)\,(1/T) + \ln(A)$

For A → B, k_{for} is 0.003/min at 25 °C and 0.025/min at 35 °C.

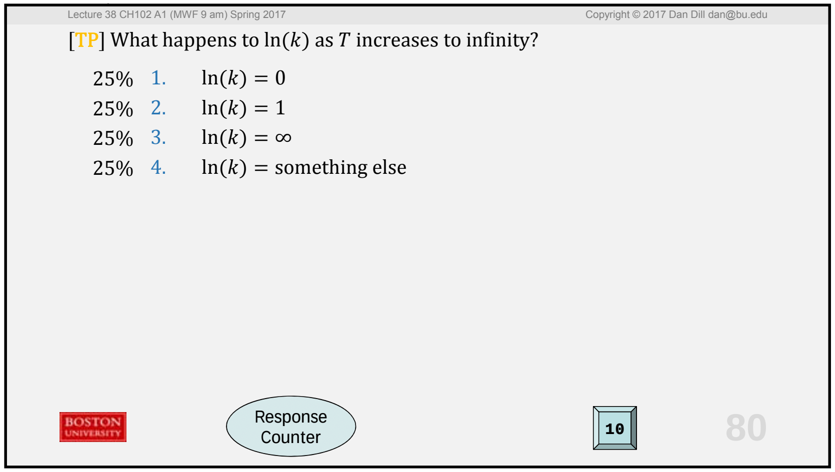
$$\text{slope} = -E_a/R = (\ln(k_{A,2}) - \ln(k_{A,1}))\,/(1/T_2 - 1/T_1) = -19000$$

For C → D, k_{for} is 0.003/min at 25 °C and 0.035/min at 35 °C.

$$\text{slope} = -E_a/R = (\ln(k_{C,2}) - \ln(k_{C,1}))\,/(1/T_2 - 1/T_1) = -23000$$



Putting it all together:
First law, second law, equilibrium, and kinetics



[TP] What happens to $\ln(k)$ as T increases to infinity?

25% 1. $\ln(k) = 0$
25% 2. $\ln(k) = 1$
25% 3. $\ln(k) = \infty$
25% 4. $\ln(k)$ = something else

Response Counter

10

First law, second law, equilibrium, and kinetics

Rate constant: $\ln(k) = -(E_a/R)(1/T) + \ln(A)$, ...

So, at very high T, $\ln(k) \longrightarrow \ln(A)$

[TP] What happens to $\ln(K)$ as T increases to infinity?

25%	1.	$\ln(K) = 0$
25%	2.	$\ln(K) = 1$
25%	3.	$\ln(K) = \infty$
25%	4.	$\ln(K) =$ something else

Response Counter

10

First law, second law, equilibrium, and kinetics

Rate constant: $\ln(k) = -(E_a/R)(1/T) + \ln(A)$, ...

so, at very high T, $\ln(k) \longrightarrow \ln(A)$

Equilibrium constant: $\ln(K) = -(\Delta H°/R)(1/T) + \Delta S°/R$, ...

so, at very high T, $\ln(K) \longrightarrow \Delta S°/R$

What's the connection?

First law, second law, equilibrium, and kinetics

Rate constant: $\ln(k) = -(E_a/R)(1/T) + \ln(A)$, ...

so, at very high T, $\ln(k) \longrightarrow \ln(A)$

Equilibrium constant: $\ln(K) = -(\Delta H°/R)(1/T) + \Delta S°/R$, ...

so, at very high T, $\ln(K) \longrightarrow \Delta S°/R$

Since $K = k_{\text{for}}/k_{\text{rev}}$, we see that at very high T, ...

$\ln(K) \longrightarrow \ln(A_{\text{for}}/A_{\text{rev}})$

First law, second law, equilibrium, and kinetics

$$\lim_{T\to\infty}\ln(K)=\frac{\Delta S^\circ}{R}=\lim_{T\to\infty}\ln\left(\frac{k_{for}}{k_{rev}}\right)=\ln\left(\frac{A_{for}}{A_{rev}}\right)$$

What is the significance of this result?

First, at very high T, K only depends on $\Delta S^\circ = \Delta S^\circ{}_{\text{sys}}$.

This is because at very high T, heat flow can no longer change entropy of the surroundings,

$$\Delta S_{\text{sur}} = -\frac{\Delta H^\circ{}_{\text{sys}}}{T} = \frac{\Delta H^\circ{}_{\text{sys}}}{\infty} = 0$$

First law, second law, equilibrium, and kinetics

$$\lim_{T\to\infty}\ln(K)=\frac{\Delta S^\circ}{R}=\lim_{T\to\infty}\ln\left(\frac{k_{for}}{k_{rev}}\right)=\ln\left(\frac{A_{for}}{A_{rev}}\right)$$

What is the significance of this result?

Second, since the entropy change of the system can be expressed as

$$\frac{\Delta S^\circ}{R}=\frac{1}{R}\ln\left(\frac{W_{\text{products}}}{W_{\text{reactants}}}\right)$$

at very high T, the ratio of the Arrhenius factors is related to the ratio of the number arrangements or reactants and products,

$$\lim_{T\to\infty}\ln(K)=\frac{\Delta S^\circ}{R}=\frac{1}{R}\ln\left(\frac{W_{\text{products}}}{W_{\text{reactants}}}\right)=\ln\left(\frac{A_{for}}{A_{rev}}\right)$$

First law, second law, equilibrium, and kinetics

Rate constant: $\ln(k) = -(E_{\text{a}}/R)(1/T) + \ln(A)$

Equilibrium constant: $\ln(K) = -(\Delta H^\circ/R)(1/T) + \Delta S^\circ/R$

What about when T is not very high?

What's the connection between enthalpy change and activation energies?

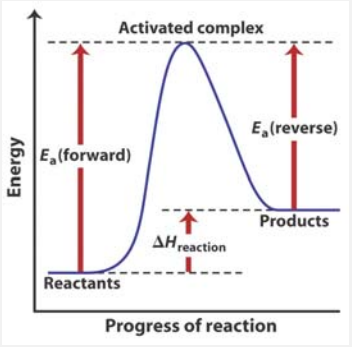
$K = k_{\text{for}}/k_{\text{rev}}$ and so …

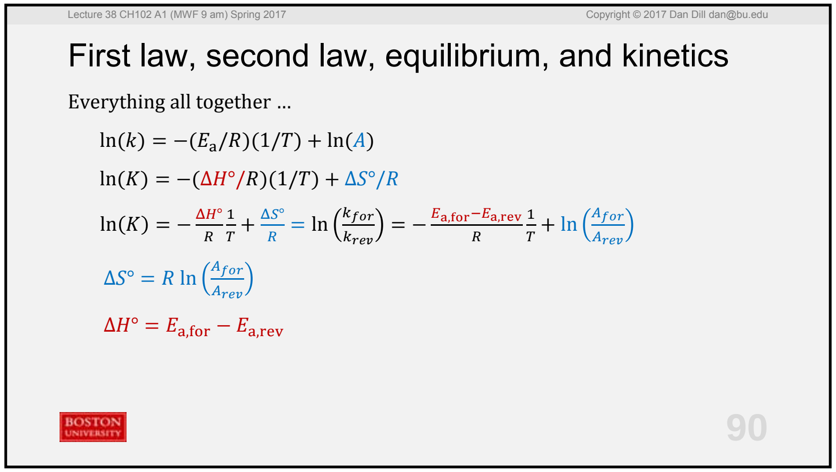
$$\ln(K) = -\frac{\Delta H^\circ}{R}\frac{1}{T}+\frac{\Delta S^\circ}{R}=\ln\left(\frac{k_{for}}{k_{rev}}\right)=-\frac{E_{\text{a,for}}-E_{\text{a,rev}}}{R}\frac{1}{T}+\ln\left(\frac{A_{for}}{A_{rev}}\right)$$

and therefore, …

$$\Delta H^\circ = E_{\text{a,for}} - E_{\text{a,rev}}$$

$\Delta H^\circ = E_{\text{a,for}} - E_{\text{a,rev}}$





First law, second law, equilibrium, and kinetics

Everything all together …

$$\ln(k) = -(E_\mathrm{a}/R)(1/T) + \ln(A)$$

$$\ln(K) = -(\Delta H°/R)(1/T) + \Delta S°/R$$

$$\ln(K) = -\frac{\Delta H°}{R}\frac{1}{T} + \frac{\Delta S°}{R} = \ln\left(\frac{k_{for}}{k_{rev}}\right) = -\frac{E_\mathrm{a,for}-E_\mathrm{a,rev}}{R}\frac{1}{T} + \ln\left(\frac{A_{for}}{A_{rev}}\right)$$

$$\Delta S° = R\ln\left(\frac{A_{for}}{A_{rev}}\right)$$

$$\Delta H° = E_\mathrm{a,for} - E_\mathrm{a,rev}$$