

Lecture 36 CH102 A2 (MWF 11:15 am) Spring 2019 Copyright © 2019 Dan Dill dan@bu.edu

[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. $\ln(k) = \text{something else}$

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Response Counter

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 Wednesday, May 1, 2019

- Complete: Rate versus temperature: E_a and A .
- Evaluation: bu.campuslabs.com/courseeval
- Equilibrium versus temperature
- First law, second law, equilibrium, and kinetics

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Rate versus temperature

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

E_a is activation energy
 A is frequency factor

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

$$\ln(k) = -\frac{E_a}{R} \frac{1}{T} + \ln(A)$$

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

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

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

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

Slope = $-E_a/R$

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

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

An example to try:

$k_1 = 43.0 \times 10^{-5}/\text{min}$, $T_1 = 45^\circ\text{C}$

$k_2 = 3.38 \times 10^{-5}/\text{min}$ at $T_2 = 25^\circ\text{C}$

slope $\rightarrow -12.1 \times 10^3 \text{ K}$

$E_a \rightarrow -\text{slope } R = +100. \text{ kJ/mol}$

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Online course evaluation

- bu.campuslabs.com/courseeval
- Use BU login and Kerberos password
- Anonymous and seen by instructors only after grades submitted
- Comments in text fields especially valued and encouraged.
- Please try to answer all questions
- When done, please close your browser

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Equilibrium versus temperature

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

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

$$\text{slope} = -E_a/R = \frac{\ln(k_{A2}) - \ln(k_{A1})}{1/T_2 - 1/T_1} = -19000 \text{ K}$$

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

$$\text{slope} = -E_a/R = \frac{\ln(k_{C2}) - \ln(k_{C1})}{1/T_2 - 1/T_1} = -23000 \text{ K}$$

The larger E_a , the greater the temperature dependence.

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[TP] The forward activation energy of an exothermic reaction must be ...

- 25% 1. smaller than its reverse activation energy
- 25% 2. the same as its reverse activation energy
- 25% 3. larger than its reverse activation energy
- 25% 4. More information needed

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[TP] The forward activation energy of an exothermic reaction is **smaller** than its reverse activation energy. This means that, compared to k_{rev} , k_{for} for an exothermic reaction increases with temperature ...

- 0% 1. more slowly
- 0% 2. by the same amount
- 0% 3. more rapidly
- 0% 4. More information needed

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[TP] We know all rate constants, k , increase with increased temperature. We also know equilibrium constants are related to rate constants as the ratio $K = k_{\text{for}}/k_{\text{rev}}$. This means that as temperature increases the equilibrium constant K will ...

- 0% 1. increase
- 0% 2. not change
- 0% 3. decrease
- 0% 4. More information needed

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[TP] We know all rate constants, k , increase with increased temperature. We also know equilibrium constants are related to rate constants as the ratio $K = k_{\text{for}}/k_{\text{rev}}$. For exothermic reactions, k_{for} increases with temperature more slowly than k_{rev} , since the **forward activation energy is smaller** than the reverse activation energy. This means that as temperature increases **the equilibrium constant, K , of an exothermic reaction will ...**

25% 1. increase
 25% 2. not change
 25% 3. decrease
 25% 4. More information needed

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[TP] The forward activation energy of an endothermic reaction must be ...

25% 1. smaller than its reverse activation energy
 25% 2. the same as its reverse activation energy
 25% 3. larger than its reverse activation energy
 25% 4. More information needed

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[TP] We know all rate constants, k , increase with increased temperature. We also know equilibrium constants are related to rate constants as the ratio $K = k_{\text{for}}/k_{\text{rev}}$. For endothermic reactions, k_{for} increases with temperature more rapidly than k_{rev} , since the **forward activation energy is larger**. This means that as temperature increases **the equilibrium constant, K , of an endothermic reaction will ...**

25% 1. increase
 25% 2. not change
 25% 3. decrease
 25% 4. More information needed

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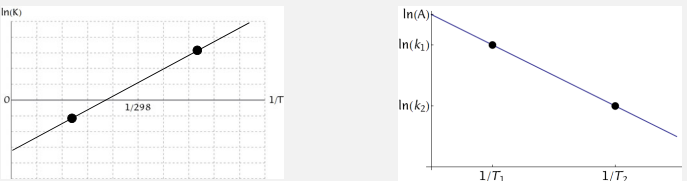
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Putting it all together:
First law, second law, equilibrium, and kinetics

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$$\ln(K) = -\left(\frac{\Delta H^\circ}{R}\right)\frac{1}{T} + \frac{\Delta S^\circ}{R}$$

$$\ln(k) = -\left(\frac{E_a}{R}\right)\frac{1}{T} + \ln(A)$$


$K = \frac{k_{\text{for}}}{k_{\text{rev}}}$

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First law, second law, equilibrium, and kinetics

Rate constant: $\ln(k) = -\left(\frac{E_a}{R}\right)\frac{1}{T} + \ln(A)$, ...

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

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

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First law, second law, equilibrium, and kinetics

$$\text{Rate constant: } \ln(k) = -\left(\frac{E_a}{R}\right)\frac{1}{T} + \ln(A), \dots$$

$$\text{so, at very high } T, \ln(k) \rightarrow \ln(A)$$

$$\text{Equilibrium constant: } \ln(K) = -\left(\frac{\Delta H^\circ}{R}\right)\frac{1}{T} + \frac{\Delta S^\circ}{R}, \dots$$

$$\text{so, at very high } T, \ln(K) \rightarrow \frac{\Delta S^\circ}{R}$$

What's the connection?



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First law, second law, equilibrium, and kinetics

$$\text{Rate constant: } \ln(k) = -\left(\frac{E_a}{R}\right)\frac{1}{T} + \ln(A), \dots$$

$$\text{so, at very high } T, \ln(k) \rightarrow \ln(A)$$

$$\text{Equilibrium constant: } \ln(K) = -\left(\frac{\Delta H^\circ}{R}\right)\frac{1}{T} + \frac{\Delta S^\circ}{R}, \dots$$

$$\text{so, at very high } T, \ln(K) \rightarrow \frac{\Delta S^\circ}{R}$$

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

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



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First law, second law, equilibrium, and kinetics

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

What is the significance of this result?



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First law, second law, equilibrium, and kinetics

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

What is the significance of this result?

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

Why is this?

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

$$\lim_{T \rightarrow \infty} \Delta S_{\text{sur}} = -\lim_{T \rightarrow \infty} \frac{\Delta H^\circ_{\text{sys}}}{T} = -\frac{\Delta H^\circ_{\text{sys}}}{\infty} = 0$$



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First law, second law, equilibrium, and kinetics

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

What is the significance of this result?

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

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

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

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



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[Group Quiz] We've established that as T increases to infinity,

$$\ln(K) = \ln\left(\frac{k_{for}}{k_{rev}}\right) = \ln\left(\frac{A_{for}}{A_{rev}}\right)$$

Therefore at $T = \infty$, the equilibrium constant must depend on the ...

- 0% 1. entropy change of the surroundings
- 0% 2. entropy change of the system
- 0% 3. enthalpy change of the surroundings
- 0% 4. enthalpy change of the system
- 0% 5. (1) and (2) are correct
- 0% 6. (2) and (4) are correct
- 0% 7. Further information needed

Response
Counter

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