

[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

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Response Counter

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Lecture 38 CH102 A2 (MWF 11:15 am)

Wednesday, May 2, 2018

- Evaluation: bu.campuslabs.com/courseeval
- First law, second law, equilibrium, and kinetics

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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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Putting it all together:

First law, second law, equilibrium, and kinetics

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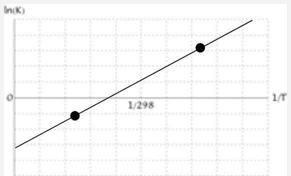
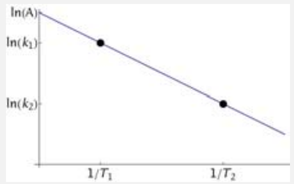
$$\ln(K) = -\left(\frac{\Delta H°}{R}\right)\frac{1}{T} + \frac{\Delta S°}{R}$$

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





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

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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

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

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

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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

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

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

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

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

What's the connection?

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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, $\ln(k) \longrightarrow \ln(A)$

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

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

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

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

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First law, second law, equilibrium, and kinetics

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

What is the significance of this result?

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First law, second law, equilibrium, and kinetics

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

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,

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

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First law, second law, equilibrium, and kinetics

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

What is the significance of this result?

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

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

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

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

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First law, second law, equilibrium, and kinetics

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

Equilibrium constant: $\ln(K) = -\left(\frac{\Delta H°}{R}\right)\frac{1}{T} + \frac{\Delta S°}{R}$

What about when T is not very high?

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First law, second law, equilibrium, and kinetics

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

Equilibrium constant: $\ln(K) = -\left(\frac{\Delta H°}{R}\right)\frac{1}{T} + \frac{\Delta S°}{R}$

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

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

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

and therefore, …

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

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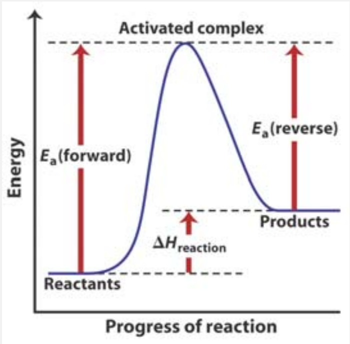
$\Delta H° = E_{\text{a,for}} - E_{\text{a,rev}}$



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

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

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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First law, second law, equilibrium, and kinetics

Everything all together …

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

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

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

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

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

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