

Lecture 33 CH102 A1 (MWF 9:05 am) Spring 2019 Copyright © 2019 Dan Dill dan@bu.edu

[TP] What do we need to know to sketch
 $\ln(K) = -\Delta H^\circ/R(1/T) + \Delta S^\circ/R$?

17% 1. How K changes with T
 17% 2. The sign of ΔH°
 17% 3. The sign of ΔS°
 17% 4. All of the above
 17% 5. Either (1), or (2) and (3)
 17% 6. Some other factor(s)

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Response Counter

10

1

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 Wednesday, April 24, 2019

- ΔG , E , ΔH , ΔS , Q , K , and T

Next lecture: Begin ch18: Definition of "rate"; rate versus [...] from experiment; making sense of rate versus [...]: Reaction mechanisms

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Using temperature to change equilibrium: K versus T
 ΔG , E , ΔH , ΔS , Q , K , and T

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13

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ΔG , ΔH , ΔS , E , Q , K , and T

Rearranging

$$\Delta G = -n_e F E_{\text{cell}} = RT \ln(Q/K) = \Delta H - T\Delta S$$

we see that this means

$$E_{\text{cell}} = -\left(\frac{RT}{n_e F}\right) \ln(Q/K) = -\left(\frac{RT}{n_e F}\right) 2.303 \log\left(\frac{Q}{K}\right)$$

using $x = 10^{\log(x)}$,

and so that $\ln(x) = \ln(10) \log(x) = 2.303 \log(x)$

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15

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ΔG , ΔH , ΔS , E , Q , K , and T

$$E_{\text{cell}} = -\left(\frac{RT}{n_e F}\right) \ln(Q/K) = -\left(\frac{RT}{n_e F}\right) 2.303 \log\left(\frac{Q}{K}\right)$$

At 25 °C

$$\left(\frac{RT}{n_e F}\right) = \left(\frac{R \cdot 298.15\text{K}}{n_e F}\right) 2.303 = \frac{0.05912}{n_e} \text{V} \approx \frac{0.06}{n_e} \text{V}$$

and so at 25 °C

$$E_{\text{cell}} \approx -\frac{0.06}{n_e} \text{V} \log\left(\frac{Q}{K}\right) \text{ and } E^\circ_{\text{cell}} \approx \frac{0.06}{n_e} \text{V} \log(K)$$

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ΔG , ΔH , ΔS , E , Q , K , and T

$$\Delta G = -nFE_{\text{cell}} = RT \ln(Q/K) = \Delta H - T\Delta S$$

How about for **standard states**?

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = RT \ln(1/K) = \Delta H^\circ - T\Delta S^\circ$$

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Connection between T and K

$$RT \ln(1/K) = \Delta H^\circ - T\Delta S^\circ$$

For values of T near 298 K, ΔH° and ΔS° are **nearly constant**.
What does this tell us about the graph of $\ln(K)$ versus $1/T$?

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Connection between T and K

Rearrange $RT \ln(1/K) = \Delta H^\circ - T\Delta S^\circ$ into the equation

$$y = mx + b \text{ with}$$

$$y = \ln(K)$$

$$x = 1/T \dots$$

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

$$y = m x + b$$

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Connection between T and K

What do we need to make a sketch of $y = \ln(K) = -\Delta H^\circ/R(1/T) + \Delta S^\circ/R$ versus $x = 1/T$ for the process **steam** \rightarrow **water**?

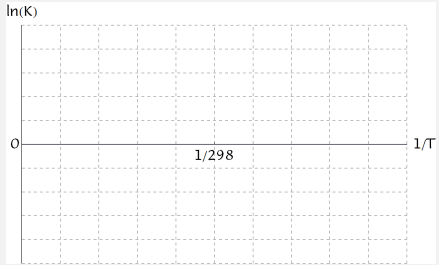
Can we get what we need to make the sketch?

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Connection between T and K

Make a sketch of $y = \ln(K) = -\Delta H^\circ/R(1/T) + \Delta S^\circ/R$ versus $x = 1/T$ for the process **steam** \rightarrow **water**. If it crosses the $1/T$ axis, specify where relative to $1/(298 \text{ K})$.



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[TP] For the reaction $\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l)$, at what temperature range will result in the **greatest amount of products (largest K)**?

25% 1. Very low T (large $1/T$)
 25% 2. Very high T (small $1/T$)
 25% 3. The amount will be the same at all T
 25% 4. More information needed

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[TP] For the reaction $2 \text{H}_2\text{O}(g) \rightarrow 2 \text{H}_2(g) + \text{O}_2(g)$, what temperature range will result in the **greatest amount of products (largest K)**?

- 25% 1. Very low T (large $1/T$)
 25% 2. Very high T (small $1/T$)
 25% 3. The amount will be the same at all T
 25% 4. More information needed



Response Counter



24

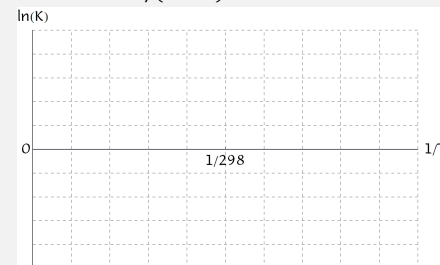
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Connection between T and K

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

Sketch $\ln(K)$ versus $1/T$ for $2 \text{H}_2\text{O}(g) \rightarrow 2 \text{H}_2(g) + \text{O}_2(g)$. If it crosses the $1/T$ axis, specify where relative to $1/(298 \text{ K})$.



25

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[TP] For the reaction $2 \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$, what temperature range will result in the **greatest amount of products (largest K)**?

- 25% 1. Very low T (large $1/T$)
 25% 2. Very high T (small $1/T$)
 25% 3. The amount will be the same at all T
 25% 4. More information needed



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26

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[TP] The reaction $2 \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$ is **exothermic**. What temperature range will result in the **greatest amount of products (largest K)**?

- 25% 1. Very high T (small $1/T$)
 25% 2. Very low T (large $1/T$)
 25% 3. The amount will be the same at all T
 25% 4. More information needed



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27

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[TP] The exothermic reaction $2 \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$ has the greatest amount of products (largest K) at very low T . The reason for this is that ...

17% 1. $\Delta_r H^\circ < 0$ and so K increases as T is decreased.

17% 2. heat is a "product" so removing heat (decreasing T) shifts equilibrium to products

17% 3. $\Delta_r S^\circ < 0$

17% 4. 1, 2 and 3

17% 5. 1 and 3

17% 6. Something else

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[TP] A certain chemical reaction is **not spontaneous** when $Q = 1$ at 300 K. The **entropy change** for the reaction is **+130 J/K**. The reaction **must be** ...

25% 1. endothermic

25% 2. exothermic

25% 3. neither ($\Delta H = 0$)

25% 4. More information needed

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[TP] A chemical reaction is **endothermic** and has $\Delta S_{\text{sys}} < 0$. This means the reaction **will be spontaneous** when $Q = 1$...

0% 1. only at low temperature

0% 2. only at high temperature

0% 3. always

0% 4. never

0% 5. Further information required

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[Quiz] At 300 K, when $Q = 1$ hydrogen burns vigorously in oxygen to form water. At **very high temperature**, water will ...

33% 1. will not decompose into H_2 and O_2

33% 2. decompose into H_2 and O_2

33% 3. More information needed

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