

Lecture 27 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2016 Dan Dill dan@bu.edu

[TP] A redox reaction has  $K = 10$ . If there are **only reactants** present,  $-\log(Q/K)$  is ...

17% 1.  $+\infty$   
17% 2. 2  
17% 3. 1  
17% 4. 0  
17% 5. -1  
17% 6.  $-\infty$

## Lecture 27 CH102 A1 (MWF 9:05 am)

Monday, April 3, 2017

- Complete: Cell voltage versus spontaneity.
- The Nernst equation.

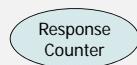
Next lecture: Complete ch16: Exploring the Nernst equation.  
Concentration cells: Mixing → electric current



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[TP] A redox reaction has  $K = 10$ . If there are **only reactants** present,  $-\log(Q/K)$  is ...

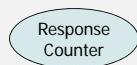
17% 1.  $+\infty$   
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[Quiz] For the redox process  
 $\text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq)$   
when  $[\text{Cu}^{2+}] = 0.001$  and  $[\text{Zn}^{2+}] = 0$ , the voltage is ...

33% 1.  $< 0$   
33% 2. 0  
33% 3.  $> 0$

## Voltage $E$ versus $Q/K$

Make a table of  $Q$ ,  $Q/K$  and  $-\log(Q/K)$  for a reaction with  $K = 10$ , for values  $Q = 0, 0.1, 1, 10, 100$ , and  $\infty$ .

$Q$	$Q/K$	$-\log(Q/K)$
0	0	$+\infty$
0.1	0.01	2
1	0.1	1
10	1	0
100	10	-1
$\infty$	$\infty$	$-\infty$

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## Voltage $E$ versus $Q/K$

Make a table of  $Q$ ,  $Q/K$  and  $-\log(Q/K)$  for a reaction with  $K = 10$ , for values  $Q = 0, 0.1, 1, 10, 100$ , and  $\infty$ .

$Q$	$Q/K$	$-\log(Q/K)$
0	0	$+\infty$
0.1	0.01	2
1	0.1	1
10	1	0
100	10	-1
$\infty$	$\infty$	$-\infty$

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## Voltage $E$ versus $Q/K$

Using your table, **sketch**  $-\log(Q/K)$  versus  $Q/K$ , with  $K = 10$ , for values  $Q = 0, 0.1, 1, 10, 100$ , and  $\infty$ .

$Q$	$Q/K$	$-\log(Q/K)$
0	0	$+\infty$
0.1	0.01	2
1	0.1	1
10	1	0
100	10	-1
$\infty$	$\infty$	$-\infty$

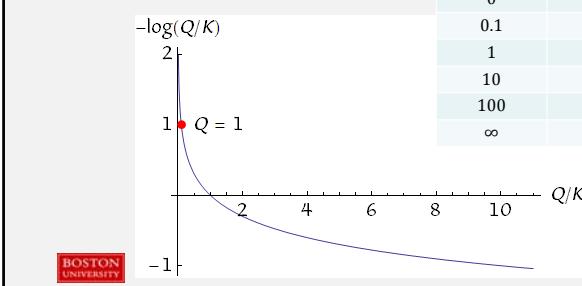
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## Voltage $E$ versus $Q/K$

Using your table, **plot**  $-\log(Q/K)$  versus  $Q/K$ , with  $K = 10$ , for values  $Q = 0, 0.1, 1, 10, 100$ , and  $\infty$ .

$Q$	$Q/K$	$-\log(Q/K)$
0	0	$+\infty$
0.1	0.01	2
1	0.1	1
10	1	0
100	10	-1
$\infty$	$\infty$	$-\infty$



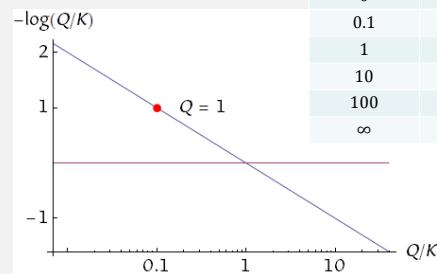
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## Voltage $E$ versus $Q/K$

Using your table, plot  $-\log(Q/K)$  versus  $Q/K$ , with  $K = 10$ , for values  $Q = 0, 0.1, 1, 10, 100$ , and  $\infty$ .

$Q$	$Q/K$	$-\log(Q/K)$
0	0	$+\infty$
0.1	0.01	2
1	0.1	1
10	1	0
100	10	-1
$\infty$	$\infty$	$-\infty$



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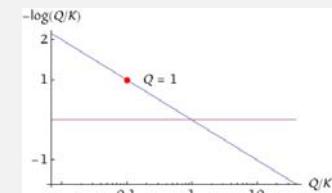
## Voltage $E$ versus $Q/K$

We have discovered that  $-\log(Q/K)$  behaves as we expect voltage  $E$  to behave versus  $Q/K$

We will learn that at 25 °C, the constant of proportionality is  $-(0.06/n_e)$ , so that

$$E = -(0.06/n_e) V \log(Q/K)$$

in terms of the number of moles  $n_e$  of electrons transferred per reaction unit.



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$$E = -(0.06/n_e) V \log(Q/K)$$

Calculate the voltage at 25 °C for  $n_e = 1$  when  $Q = (1/100) \times K$

$$E = 0.12 \text{ V}$$



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$$E = -(0.06/n_e) V \log(Q/K)$$

Calculate the voltage at 25 °C for  $n_e = 1$  when  $Q = (1/10) \times K$

$$E = 0.06 \text{ V}$$



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$$E = -(0.06/n_e) V \log(Q/K)$$

Calculate the voltage at 25 °C for  $n_e = 1$  when  $Q = (10) \times K$

$$E = -0.06 V$$

$$E = -(0.06/n_e) V \log(Q/K)$$

At 25 °C for  $n_e = 1$ , ...  
each **order of magnitude** change in  $Q/K$  ...  
changes voltage by **0.06 V**.

$$E = -(0.06/n_e) V \log(Q/K)$$

Write an expression for  $E$  when  $Q = 1$ .

$$E = -(0.06/n_e) V \log(Q/K)$$

The value of  $E$  when  $Q = 1$  is called the **standard voltage** and at 25 °C is written as

$$E(Q=1) = E^\circ = +(0.06/n_e) V \log(K)$$

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**[TP]** The value of  $E$  when  $Q = 1$  at 25 °C is

$$E(Q=1) = E^\circ = +(\ 0.06/n_e) V \log(K)$$

For  $n_e = 1$ , if  $K$  is different by a factor of ten (say, 17 instead of 1.7), the magnitude of standard voltage will change by ...

- 20% 1. 10 V  
 20% 2. 1 V  
 20% 3. 0.1 V  
 20% 4. 0.06 V  
 20% 5. Some other amount

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**[TP]** The value of  $E$  when  $Q = 1$  at 25 °C is

$$E(Q=1) = E^\circ = +(\ 0.06/n_e) V \log(K)$$

For  $n_e = 3$ , if  $K$  is different by a factor of ten (say, 17 instead of 1.7), the magnitude of standard voltage will change by ...

- 25% 1. 0.18 V  
 25% 2. 0.06 V  
 25% 3. 0.02 V  
 25% 4. Some other amount

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**[Quiz]** The value of  $E$  when  $Q = 1$  at 25 °C is

$$E(Q=1) = E^\circ = +(\ 0.06/n_e) V \log(K)$$

A typical physiological value of  $E^\circ$  is 0.18 V.For  $n_e = 1$  this corresponds to the value of  $K$  equal to ...

- 17% 1. 0.1  
 17% 2. 1  
 17% 3. 10  
 17% 4. 100  
 17% 5. 1000  
 17% 6. Some other value

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$$E = -(0.06/n_e) V \log(Q/K)$$

The value of  $E$  when  $Q = 1$  at 25 °C is

$$E(Q=1) = E^\circ = +(\ 0.06/n_e) V \log(K)$$

Calculate  $K$  corresponding to  $E^\circ = 1.8$  V for  $n_e = 1$ .
 $K = 10^{30}$ . Very large!
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$$E = -(0.06/n_e) V \log(Q/K)$$

The value of  $E$  when  $Q = 1$  at 25 °C is

$$E(Q=1) = E^\circ = +(0.06/n_e) V \log(K)$$

Express the cell voltage for **any value of  $Q$**  in terms of  $E^\circ$ , that is, in term of the cell voltage when  $Q = 1$ .

$$E = -(0.06/n_e) V \log(Q/K)$$

The value of  $E$  when  $Q = 1$  at 25 °C is

$$E(Q=1) = E^\circ = +(0.06/n_e) V \log(K)$$

The cell voltage at 25 °C for **any value of  $Q$**  in terms of the cell voltage when  $Q = 1$  is

$$E(\text{any } Q) = E^\circ - (0.06/n_e) V \log(Q)$$

This is called the **Nernst equation**