

Nernst Equation

From previous Factsheets you will remember that:

- The standard electrode potential of a cell can be calculated from the standard electrode potentials of the half cells from which it is made.
- The standard electrode potential of a half cell is the electromotive force (e.m.f.) or voltage measured under standard conditions when the half-cell is connected to a standard hydrogen electrode.

The standard conditions are concentrations of solutions at 1.00 mol dm⁻³, temperature of 298 K and pressure of 100 kPa. When these conditions are not standard, the e.m.f. of a cell will change.

Qualitative predictions about how the electrode potential under non-standard conditions will change can be made using le Chatelier's Principle.

However, the Nernst equation can be used to calculate the electrode potential of a cell that is not under standard conditions. It is perhaps the most important equation in electrochemistry and relates the electrode potential of a cell under non-standard conditions to the standard electrode potential, the temperature and the concentrations of the chemical species that are undergoing oxidation and reduction.

It can be applied to a full cell reaction or a half cell.

Walther Nernst was born in what is now Poland and helped to establish the field of physical chemistry. He is best known for the developing the equation that now bears his name.

The Equation

One form of the equation is shown below.

This considers how the electrode potential for a full cell (E_{cell}) is related to the standard electrode potential, the concentration of the species undergoing oxidation and reduction and the temperature.

Figure 1

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{zF} \ln \frac{[\text{reduced species}]}{[\text{oxidised species}]}$$

where:

- R = the gas constant (8.314 J K⁻¹ mol⁻¹)
- T = the temperature in K
- z = number of electrons being transferred in the reaction
- F = the Faraday constant (9.65 x 10⁴ C mol⁻¹)
- [oxidised species] = the concentration of the species with the higher oxidation state
- [reduced species] = the concentration of the species with the lower oxidation state

In some examination specifications such as the IB, another form of the Nernst equation is used involving Q_r , the reaction quotient. The reaction quotient can be used as a direct replacement for the fraction in the equation given in **Figure 1** (i.e., is the ratio of the concentrations of the reduced species and oxidised species).

Figure 2

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{zF} \ln Q_r$$

The form of the equation given in **Figure 2** (using Q_r) can be used to determine the overall cell potential for a system (such as a voltaic cell) under non-standard conditions. In this case the reaction quotient is calculated in the same manner as K_c using the overall redox equation to determine products and reactants of the cell (see example below).

Some A level examination specifications (for example C.I.E) use \log_{10} instead of \ln and combine the constants. This, together with maintaining the temperature at a constant 298 K changes the equation to **Figure 3**:

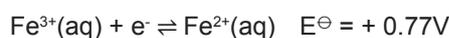
$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} + \frac{0.059}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

Using this form of the equation, the effect of changing the temperature on the electrode potential cannot be determined.

Worked examples

Example 1

Consider the half equation:



Since this is under standard conditions, this value of E^{\ominus} only applies when the concentrations of Fe^{3+} and Fe^{2+} are 1.00 mol dm⁻³.

If the concentration of Fe^{2+} is lowered to 0.10 mol dm⁻³ (and the temperature is kept at 298 K) we can predict from le Chatelier's Principle that the equilibrium will move to the right hand side to counteract the change made and the value of E will become more positive.

Using the form of the Nernst equation in **Figure 3** we can calculate the electrode potential under the non-standard conditions.

$$[\text{oxidised species}] = [\text{Fe}^{3+}] = 1.00 \text{ mol dm}^{-3}$$

$$[\text{reduced species}] = [\text{Fe}^{2+}] = 0.10 \text{ mol dm}^{-3}$$

$$z = \text{number of electrons transferred} = 1$$

Figure 4

$$E_{cell} = E_{cell}^{\ominus} + \frac{0.059}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

$$E_{cell} = 0.77 + \frac{0.059}{1} \log \frac{1.00}{0.10}$$

$$= 0.83 \text{ V}$$

So, as predicted by le Chatelier's principle, the value of E_{cell} when the concentration of Fe^{2+} ions was lowered became more positive.

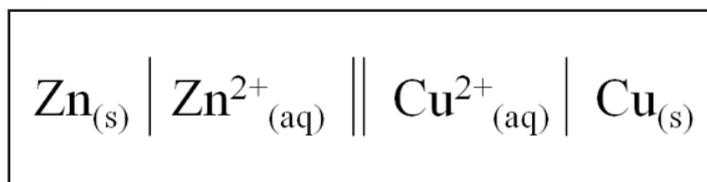
Note: For ease of use, we have been discussing species in terms of their concentration. However, when you have a solid substance like a metal, you cannot use the term concentration. The more accurate term to use is activity. The chemical activity is defined as a measure of the effective concentration of a species. For reasons beyond the scope of this Factsheet, a metal is defined as having an activity (or effective concentration) of 1.

You will need to use this idea in the questions at the end of the Factsheet.

Example 2

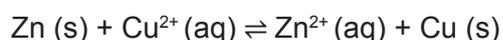
Consider the electrochemical cell shown below.

Figure 5



The standard electrode potential for this cell, E^{\ominus} , is +1.10V

The equation for the reaction can be obtained by combining the 2 half equations to give:



$$Q_r = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

The activities of solid zinc and copper are equal to 1 so can be ignored for the purposes of the calculation. Under standard conditions, the concentrations of the salt solutions are 1.00 mol dm⁻³ and therefore $Q_r = 1$. If the concentrations are not standard, the form of the Nernst equation in **Figure 2** can be used to determine the cell potential.

Calculate the cell potential at 298 K when $[\text{Zn}^{2+}] = 0.10 \text{ mol dm}^{-3}$ and $[\text{Cu}^{2+}] = 1.50 \text{ mol dm}^{-3}$.

$z = 2$ (since there are 2 electrons involved in the reaction)

Figure 6

$$Q_r = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{0.1}{1.5} = 0.0667$$

$$E_{cell} = E_{cell}^{\ominus} - \frac{RT}{zF} \ln Q_r$$

$$= +1.13 \text{ V}$$

This is entirely consistent with le Chatelier's Principle which predicts that an increase in the concentration of the Cu^{2+} ions and a decrease in the concentration of the Zn^{2+} will favour the forward reaction, shifting the equilibrium to the right hand side and therefore increasing the cell potential.

Using the Nernst Equation in biological applications

The Nernst equation is frequently used in biological situations to calculate the membrane potential (that is the difference in potential between the inside and the outside of a cell membrane). Cellular membranes have a different concentration of ions either side of them and it is important that these concentrations are carefully maintained so that transport of substances across the membrane occurs. In addition, the changing of the membrane potential in nerve cells is the means by which a nerve impulse is generated and spread through the body.

Figure 7 shows the relationship between the membrane potential with respect to ion X (V_x) and the concentration of ion X outside, $[X]_o$, and inside, $[X]_i$, the cell. Its similarity with the Nernst equation in **Figure 1** is obvious. This time z refers to the charge of the ion, for example if considering sodium or potassium ions, $z = +1$ or if considering chloride ions, $z = -1$.

Figure 7

$$V = \frac{RT}{zF} \ln \frac{[X]_o}{[X]_i}$$

Worked Example

Calculate the membrane potential of a cell under the following conditions:

$[\text{K}^+]_{\text{outside}}$	= 80 mmol dm ⁻³
$[\text{K}^+]_{\text{inside}}$	= 160 mmol dm ⁻³
Temperature	= 37 °C

Note that the concentrations are given in mmol dm⁻³. This need not be converted to mol dm⁻³ because we are taking the logarithm of the ratio of the two concentrations. However, the temperature is given in degrees Celsius and will need to be converted to Kelvin.

276. Nernst Equation

Using the following values, the membrane potential can be calculated:

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 310 \text{ K}$$

$$z = \text{charge of ion} = +1$$

$$F = 9.65 \times 10^4 \text{ C mol}^{-1}$$

$$[X]_o = 80 \text{ mmol dm}^{-3}$$

$$[X]_i = 160 \text{ mmol dm}^{-3}$$

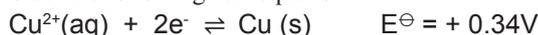
Figure 8

$$\begin{aligned} V &= \frac{8.31 \times 310}{+1 \times 96500} \ln \frac{80}{160} \\ &= -0.0185 \text{ V} \\ &= -18.5 \text{ mV} \end{aligned}$$

The membrane potential of cells is usually expressed in mV.

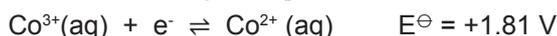
Questions

1. Consider the following half equation:



- (a) Using le Chatelier's Principle, predict and explain the effect on the electrode potential of decreasing the concentration of Cu^{2+} ions.
- (b) Using the form of the Nernst equation in **Figure 2**, calculate the electrode potential if the concentration of the Cu^{2+} ions is decreased to 0.50 mol dm^{-3} (remember the effective concentration of $\text{Cu}(\text{s}) = 1$).

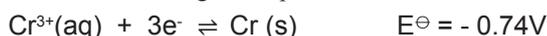
2. Consider the following half equation:



Using the Nernst equation shown in **Figure 1**, calculate the electrode potential of the half cell at 65°C when the concentration of Co^{3+} ions = 1.75 mol dm^{-3} and the concentration of Co^{2+} ions = 0.20 mol dm^{-3} .

- $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
- $F = 9.65 \times 10^4 \text{ C mol}^{-1}$

3. Consider the following half equation:



The concentration of the Cr^{3+} ions was changed. The electrode potential was measured at the same temperature and found to be -0.77 V .

- (a) Suggest, with an explanation, whether the concentration of Cr^{3+} ions was increased or decreased.
- (b) Using the Nernst equation in **Figure 3**, calculate the concentration of Cr^{3+} ions needed to produce an electrode potential of -0.77 V .
4. Using **Figure 7**, calculate the membrane potential of a cell with respect to chloride ions, given that the concentration of chloride ions inside the cell is 42 mmol dm^{-3} and the concentration outside the cell is 78 mmol dm^{-3} . The temperature of the cell is 37°C .

Answers

1. (a) As the concentration of the Cu^{2+} ions decreases, the equilibrium shifts to the left to counteract the change, so the value of the electrode potential will become less positive/decrease.
- (b) 0.33 V (remember $z = 2$)
2. 1.87 V (remember to convert the temperature to K and $z = 1$. This time you are using the \ln expression)
3. (a) The electrode potential has become more negative so the equilibrium must have shifted to the left hand side, so the concentration of Cr^{3+} ions must have been decreased.
- (b) 0.03 mol dm^{-3} .
Since the temperature is the same as the standard temperature, we can use the form of the Nernst equation in **Figure 3**. Using $z = 3$ and substituting in the values for standard electrode potential and the electrode potential of -0.77V and rearranging the equation gives the value of the concentration of Cr^{3+} ions as 0.03 mol dm^{-3} .
4. -16.5 mV
Remember to convert the temperature to K and use the value of z as -1 (the valency of the chloride ion).

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